JP, 3317668, B

JAPANESE [JP,3317668,B]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS

[Translation done.]

## CLAIMS

(57) [Claim(s)]
[Claim 1] In the ink for calcinating and carrying out solidification covering and forming the photocatalyst film, after carrying out spreading membrane formation on a base material front face by print processes At least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, The ink principal component whose content of the oxide particle which oxide particles which the reaction ended were consisted of and this reaction ended is 5-50-mol% of an ink principal component, Ink for photocatalyst film formation characterized by becoming considering viscosity as 10-100poise using the ink accessory constituent which consists of at least one sort in the nitrocellulose as a thickening component and the ethyl carbitol as a solvent, or butyl carbitol.
[Claim 2] The solid content in ink is ink for photocatalyst film formation according to claim 1 characterized by being 1 - 2 % of the weight.
[Claim 3] The formation approach of the photocatalyst film that the content of the titanium oxide in the photocatalyst film calcinated at the temperature of 250-850 degrees C is characterized by 10-100-mol being % after carrying out spreading membrane formation of the ink according to claim 1 or 2 on a base material front face by screen-stencil, gravure, or the intaglio-printing method.
[Claim 4] The formation approach of the photocatalyst film according to claim 3 characterized by a base material being glass.
[Claim 5] The formation approach of the photocatalyst film according to claim 4 characterized by forming the substrate layer which prevents the component used as the cause of reducing photocatalyst activity, such as alkali in a glass component, invading into the photocatalyst film, or uses as a principal component the oxide to which invasion is reduced.

[Translation done.]

## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the formation approach of the ink for photocatalyst film formation at the time of printing further the glass goods of various kinds of fields, such as sheet glass for construction building materials, such as sheet glass for cars, such as a windowpane for automobiles, a windowpane of a building, and glass of a mirror, and the thin film which had a photocatalyst function in front faces, such as ceramics and a metal, by print processes etc. especially, and a photocatalyst.
[0002]
[Description of the Prior Art] Recently, it applies for many patents aiming at use of effectiveness, such as antifouling property by the oxidative degradation by the photocatalysis of titanium oxide, or the optical induction super-hydrophilic-property reaction, a hydrophilic property, and fog resistance.
[0003] As a coating solution presentation of the photocatalyst film, the application (JP,8-164334,A) about a titania particle distribution solution, the application (JP,8-299789,A) about Ti alkoxide / alcoholic system, etc. are known, for example.
[0004] Moreover, about the example of membrane formation, screen-stenciling the drug solution which WO 96/No. 13327 official report is made to carry out the reaction dissolution of titanium tetra-isopropoxide, ethyl cellulose, and the organic solvent, and is obtained, for example is indicated.
[0005]
[Problem(s) to be Solved by the Invention] In the presentation solution of hypoviscosity like a titania particle part water spray solution like the publication to said JP,8-164334,A, or a titania particle distribution alcoholic solution, condensation of phase splitting by sedimentation of a particle and a particle etc. tends to take place, and a solution cannot necessarily call it stability. Moreover, in Ti alkoxide / an alcoholic system like a publication, drug solution concentration tends to change to JP,8-299789,A that a solvent tends to evaporate. moreover, unstable [ change / the description of solutions, such as phase splitting and aggravation of spreading nature, / tend / with moisture absorption and ] — etc. — there is a problem. Moreover, these solutions are hard to be called drug solution suitable for the print processes which not necessarily need viscosity of dozens to hundreds of poise, such as screen printing.
[0006] Moreover, about a presentation WO96 / given in 13327 official reports, since liquid cannot say it as stability and ethyl cellulose is used as a thickener, membranous reinforcement has the problem of being low that the carbon which is the combustion object tends to remain in the film at the time of baking.
[0007]
[Means for Solving the Problem] As the raw material which forms the titanium oxide which makes this invention in view of the technical problem which the former requires, and discovers photocatalyst activity, At least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, the content of the oxide particle which is ink which consists of oxide particles which the reaction ended, and this reaction ended — 5-50-mol% of an ink principal component — by containing It is stabilized without the stability of ink improving extremely and also discovering the trouble in various printings etc., and printing film formation can be performed. Moreover, it is the photocatalyst film produced in this ink being equipped with the photocatalyst effectiveness, abrasion resistance, and endurance, and specifying the refractive index of a thin film, and thickness further. Excitation purity is small and a color offers the formation approach of the useful ink for photocatalyst film formation in which what has small near and a small reflection factor is obtained by the neutral color, and the photocatalyst film.
[0008] That is, after carrying out spreading membrane formation on a base material front face by print processes, it sets in the ink for calcinating and carrying out solidification covering and forming the photocatalyst film, and this invention is hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound. At least one sort in the sol of the formed titanium oxide, and the ink principal component whose content of the oxide particle which oxide particles which the reaction ended were consisted of and this reaction ended is 5-50-mol% of an ink principal component, It is characterized by being ink for photocatalyst film formation which becomes considering viscosity as 10-100poise using the ink accessory constituent which consists of at least one sort in the nitrocellulose as a thickening component and the ethyl carbitol as a solvent, or butyl carbitol.
[0009] Furthermore, this invention is characterized by the solid content in ink being 1 - 2 % of the weight. [0010] Moreover, after this invention carries out spreading membrane formation of said ink on a base material front face by screen-stencil, gravure, or the intaglio-printing method, it is characterized by the content of the titanium oxide in the photocatalyst film calcinated at the temperature of 250-850 degrees C being the formation approach of the 10-100-mol photocatalyst film which is %. [0011] Furthermore, this invention is characterized by forming the substrate layer which prevents the component used as the cause of it being characterized by a base material being glass, and reducing photocatalyst activity, such as alkali in this glass component, invading into the photocatalyst film, or uses as a principal component the oxide to which invasion is reduced. [0012]
[Embodiment of the Invention] The ink which forms the high-performance photocatalyst film of this invention consists of the raw material which forms the titanium oxide which has photocatalyst activity, a raw material which forms metallic oxides other than titanium oxide, and a metallic-oxide raw material which the reaction ended, a thickener and a solvent contain as an accessory constituent of ink further, and solidification covering can carry out in the film which make dry and calcinate and has a photocatalyst activity operation after carrying out spreading membrane formation of those ink on a base material front face after mixed adjustment.

[0013] As main raw materials of the ink which forms the titanium oxide which discovers photocatalyst activity, it is at least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, and when using the crystalline titanium oxide particle which the reaction ended, this particle also contributes to photocatalyst activity. When the above-mentioned raw material is explained, it is Ti ARUKOKIDO, For example, a titanium methoxide, titanium ethoxide, titanium propoxide, Titanium butoxide, etc. a halogen content Ti alkoxide, etc. can be used. To a halogen content Ti alkoxide and a thing a chlorine content Ti alkoxide it is not necessary to make it hydrolyze by adding water and a catalyst compared with Ti alkoxide which does not contain the other halogen, to add to ink, and to mix with ink the sol which is in a reaction process by this, and there is an advantage the pot life of ink is markedly easy coming to be alike of an advantage. In addition, Ti acetylacetonato which stabilized the above-mentioned Ti alkoxide by the acetylacetone can also be used.
[0014] Moreover, depending on the case, the sols of the titanium oxide formed of hydrolysis and the polycondensation of Ti compound may be hydrolysis and a sol of titanium oxide which was made to carry out a polycondensation and was obtained about Ti compound which consists of a Ti alkoxide or Ti acetylacetonato, and a commercial item is sufficient, for example, TA-10, TA-15 (Nissan Chemical Industries make), ATORON NTi-500 (Nippon Soda make), etc. can be used as a titanium oxide sol of a commercial item. In addition, adding stabilizing agents generally used for these things, such as hexylene glycol, does not interfere other than an acetylacetone for control of these hydrolysis and polycondensation reactions.
[0015] The metallic-oxide particle which the reaction ended can give an operation very remarkable on the stable disposition of ink, and the particle which consists of titanium oxide, silicon oxide, oxidization aluminum, a zirconium dioxide, tin oxide, etc. can be used for it, and it does not limit the shape of the shape of a particle, and a sol etc. especially about those descriptions. in order that, as for these particles either of metallic oxides other than titanium oxide and titanium oxide is sufficient as whose particles which this reaction ended and that may carry out, and may contain both and the reaction ended, a reaction may not progress further in ink — the description of ink — change can be prevented. It is because it does not have film reinforcement and cannot desire improvement in a property by particle addition less than [ 5 mol % ] to an ink principal component, if it is desirable that it is [ 5-50 mol ] % as for the content of a particle and there are than 50-mol %. [ more ] In addition, an ink principal component here shows at least one sort in the sol of the metallic oxide formed [ with at least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, and the oxide particle which the reaction ended ] of hydrolysis and the polycondensation of the metal alkoxide except a titanium metal, metal acetylacetonato, a metal organic-acid salt, and metallic compounds depending on the case. Moreover, these particles have especially the desirable silica particle that is excellent in the particle of titanium oxide which is excellent in a photocatalyst operation, and/or a water retention operation.
[0016] In addition, as a titanium oxide particle, it is ST-01 (product made from the Ishihara techno), for example as a commercial item, Especially since sufficient photocatalyst activity is acquired even if it can use both distributed solutions, such as fine particles, such as SSP-25 (Sakai Chemical Industry make), STS-01 (product made from the Ishihara techno), and CA-62 (Taki Chemical make), the crystal titanium oxide particle which these reactions ended also has a photocatalyst operation with the improvement operation in stability of ink and it calcinates at low temperature, it is desirable. In addition, since the crystal form can discover the photocatalyst activity in which ANATASU excelled the rutile, it is more desirable. As for the content of the titanium oxide in the photocatalyst film, it is desirable that it is [ 10-100 mol ] %, and it is deficient in photocatalyst activity practical less than [ 10 mol % ]. In addition, the value at the time of carrying out the presentation of the formed film to oxide conversion (mol %) is shown in mol % in the text.
[0017] Moreover, about the particle which other reactions ended, colloidal silica IPA-ST (Nissan Chemical Industries make), alumina sol -10 (Nissan Chemical Industries make), an alumina clear sol (Kawaken Fine Chemicals make), etc. can be used as a commercial item. As for especially the particle size of these particles, it is desirable to use a thing about tennm or less in the case of the base material with which a base material is characterized by the transparency of glass etc. Moreover, in order to acquire higher photocatalyst activity, the front face of a photocatalyst is formed in concave convex, and these particles are effective also in order to increase the surface area.
[0018] Moreover, it is a raw material which forms metallic oxides other than titanium oxide, The metallic-oxide particle which at least one sort and/or reaction of the sol of a metallic oxide which were formed of hydrolysis and the polycondensation of a metal alkoxide, metal acetylacetonato, a metal organic-acid salt, and metallic compounds ended can be used, and these are added by ink for the various purpose, such as improvement in photocatalyst functions, such as improvement in endurance, such as film reinforcement, chemical resistance, and adhesion, control of a refractive index, and hydrophilic maintenance nature, and control of printing nature.
[0019] As a metal which forms the metallic oxide, Si, Zr, aluminum, B, P, Sn, etc. can be used, and naphthenate, oxy-acetate, a stearate, etc. can be used as a metal alkoxide as the metal acetylacetonato which stabilized said metal alkoxides, such as these methoxides, ethoxide, propoxide, and butoxide, by the acetylacetone, and a metal organic-acid salt.
[0020] About moreover, metallic-oxide sols other than the titanium oxide which a reaction has not ended They are hydrolysis and the metallic-oxide sol which was made to carry out a polycondensation and was obtained about the organic metal compound which consists of a metal alkoxide or metal acetylacetonato. Depending on the case, a commercial item is sufficient. As a silica sol Soe Per Serra (product made from the Daihachi chemical industry), The COL coat P (made in a COL coat), ATORON NSi-500 (Nippon Soda make), etc., As a zirconia sol, NZS-30A (Nissan Chemical Industries make), AZS-A (product made from the NIPPON SHOKUBAI science industry), etc. can use the sol by HAUTO form MS-AL (product made from the Fuji chemistry), and TOKYO OHKA KOGYO etc. as alumina sol. In addition, adding stabilizing agents generally used for these things, such as hexylene glycol, does not interfere other than an acetylacetone for control of these hydrolysis and polycondensation reactions.
[0021] As for the content of the solid content in ink, it is desirable that it is 1.0 - 2.0 % of the weight in oxide conversion further again. At less than 1.0 % of the weight For example, the thickness obtained by one printing etc. becomes thin too much, and printing unevenness becomes easy to be conspicuous. If the appearance of the obtained thin film will become less desirable, a refractive index will not increase to a theoretical value further, a reflection property and a transparency property change and it exceeds 2.0 % of the weight If the thickness obtained by one printing etc. tends to become thick and is set especially to 150nm or more, it will be easy to generate a crack, and moreover, for this reason, it is for thin film reinforcement, such as traverse-proof nature and the Taber abrasiveness reinforcement, also falling. By carrying out to the 1.0 - 2.0 above-mentioned% of the weight, the homogeneous coat which does not have a crack after the last heat treatment is obtained also in the forming-membranes method the thickness immediately after printings, such as screen-stencil, gravure, and intaglio printing, etc. becomes comparatively thick. In addition, when the solid content in ink here calcinates the ink applied on the base material, it remains into the film as a film structure, and they are a titanium oxide raw material, a metallic-oxide raw material except titanium oxide, and the oxide particle that the reaction

ended.
[0022] It is because the thickening effectiveness has good flammability, of course compared with ethyl cellulose etc. and there are few residuals of the carbon component for which the membranous appearance and the film reinforcement after baking are reduced, when a nitrocellulose is used as a thickening component added to ink. Moreover [ especially ], it is JISK about grade. More than H7 (H7, H20, H60, H80, H120) has desirable form and viscosity notation of assignment with 6703, and it is because the better thickening effectiveness and printing nature are obtained. In addition, the addition of a thickening component has 5 – 25 desirable % of the weight, and viscosity of ink can be made into 10–100poise suitable for print processes, such as screen-stencil, gravure, and intaglio printing. In less than 10poise, the viscosity of ink is too low for the time of printing, ink tends to spread on the screen version, it is hard to control desiccation of the ink on a version, and good patterning is no longer obtained. Moreover, it is because the carbon of the cinder of a nitrocellulose remains, and the film will color it a yellowish brown color, the homogeneity of a film surface will be spoiled or the printing nature at the time of screen-stencil not only gets remarkably bad, but it will further become easy for mechanical [ membranous ] and chemical durability to fall into the thin film which baking finally completed, if it exceeds 100poise.
[0023] The fall of the refractive index of a thin film or endurance moreover obtained can be prevented without spoiling printing nature and the homogeneity of the thin film obtained by adjusting the class of such a nitrocellulose, an addition, and viscosity. In addition, especially as print processes, the ease of carrying out of patterning to screen-stencil is desirable.
[0024] As the solvent which melts a nitrocellulose by independent [ which is added in ink ], Solvents, such as an acetone, methyl acetate, a methyl ethyl ketone, isopropyl acetate, a diethyl ketone, the 2nd butyl acetate, methyl isobutyl ketone, isobutyl acetate, methyl cellosolve, butyl acetate, the 2nd amyl acetate, ethylcellosolve, methyl-cellosolve acetate, methyl lactate, amyl acetate, ethyl lactate, a cyclohexanone, ethylcellosolve acetate, diacetone alcohol, butyl cellosolve, butyl lactate, ethyl carbitol, butyl carbitol, 3-methoxybutanol, and 3-methoxy butyl acetate, can be used. Since especially carbitols cannot evaporate easily, when it uses as a solvent of ink, the ink by which concentration change was stabilized few is obtained. Moreover, solvents, such as aromatic series solvents, such as alcohols, such as the methanol and ethanol which are supplied, propanol, a butanol, ethylene glycol, and hexylene glycol, benzene, toluene, and a xylene, and water, can be added and used for the above-mentioned solvent for the purpose, such as concentration adjustment, from the source of Ti, or the other sources of a metallic oxide.
[0025] If ethyl carbitol, butyl carbitols, or such mixture are used as a solvent, since rapid desiccation of the ink before printing etc. can be controlled, for example, and back coats, such as printing, can dry at low temperature (about 200 degrees C) comparatively, therefore pot life will be long and a thin film will moreover dry at low temperature comparatively after printing etc. by these further again, the coat which has a uniform film surface by heat-treatment of terminal temperature is obtained.
[0026] Glass, the ceramics, a metal, etc. can be used for a base material. Moreover, a base material is soda lime glass etc. Use it and Ti alkoxides etc. and the sols other than a crystalline particle are used especially for the source of Ti of ink. Prevent the component used as the cause of reducing photocatalyst activity, such as alkali in a glass component, invading into the photocatalyst film, when forming the photocatalyst film. Or the photocatalyst film with more high photocatalyst activity is ****** by preparing the substrate film which uses as a principal component any one kind of Si, Ti, Zr, aluminum, B, P, and Sn to which invasion is reduced, or two kinds or more of the arbitration of these of oxides. The substrate film of SiO2, TiO2–SiO2, aluminum2O3–SiO2, and aluminum2O3–TiO2–SiO2 is more desirable in respect of photocatalyst activity and endurance especially. What formed membranes by approaches, such as the general membrane formation approach, for example, the dip coating method using a sol gel process, a spin coat method, the roll coat method, etc. and a CVD method, PVD, in addition to the print processes which used ink may be used for membrane formation of the substrate film. Furthermore, in the case of the substrate film containing the organic component immediately after forming membranes using print processes, a sol gel process, etc., heat treatment of 300 degrees C or more is performed once, and the effectiveness which prevents invasion of alkali etc. more becomes high by burning an organic component and considering as the oxide film.
[0027] As for the printing film using this ink, it is desirable to heat-treat below about 250 degrees C at which it is necessary to heat-treat in order to acquire the film reinforcement and photocatalyst activity according to an application, and especially a nitrocellulose burns, as mentioned above about 850 degrees C transferred to a rutile mold with low photocatalyst activity from an anatase.
[0028] Moreover, when the film with which refractive indexes differ like [ when forming the substrate film of a silica on glass and forming the photocatalyst film of a titania on it further ] is formed on a base material, compared with a base material, the excitation purity of light reflection may increase from the difference of the refractive index remarkably. For example, depending on an application which is expected non-colored glass like the windowpane for cars, the increment in this excitation purity may become a problem. It is possible to fall the increment in excitation purity to 5% or less of hardly worried level by adjusting the thickness and the refractive index of the substrate film and the photocatalyst film to this. Moreover, when coloring is rather liked like **** material, it is also possible to emphasize a reflective stimulus color tone by adjusting the thickness and the refractive index of the substrate film and the photocatalyst film similarly, and to raise design nature.
[0029]
[Example 1] The titanium tetrachloride (TiCl4) was used as the start raw material, and when making isopropyl alcohol react to this and compounding Ti-isopropoxide, the solute concentration which is made to end a reaction, with some chlorine (Cl) left, and has the combination presentation of Ti(OC3H7) xCly (x+y=4) compounded about 13% of the weight of Ti alkoxide by oxide (TiO2) conversion.
[0030] The titanium oxide particle (ST-01, product made from the Ishihara techno) which this acid chlorine content Ti alkoxide and a reaction ended as a source of titanium oxide of the photocatalyst film is used. The whole ink adds a nitrocellulose H7 (product made from a die cel) about 16% of the weight as a thickener in the solution which set colloidal silica to 90:10:0:0 (mol %). Ti alkoxide [ in ink ]: — titanium oxide particle: -- silica sol: — The solute concentration of this ink for photocatalyst film formation is become 1.6 % of the weight by oxide conversion and needed. Ethyl carbitol was added as a solvent, mixed churning was improved, and it considered as the ink for photocatalyst film formation. In addition, it was 20poise when the viscosity of ink was measured.
[0031] The base material applied to glass the solution which diluted the silica sol (the COL coat P, made in a COL coat) with ethanol to the soda lime glass plate (2mm thickness, clearance) by dipping, and carried out heating baking at 500 degrees C, and the soda lime glass which attached the silica substrate film of 100nm of thickness was used for it.
[0032] next — predetermined — a configuration — patterning — having carried out — 350 — a mesh — Dacron — a screen — a glass plate — a top — carrying — Shore hardness — HS — 61 — a squeegee — using — said — a photocatalyst — the film — formation — ** — ink — this — a silica — the film — with — glass — a base material — a front face — screen-stenciling — a

place — homogeneous — beautiful — patterning — carrying out — having had — printing — the film — obtaining — having had . Then, when heat-treatment was performed for 10 minutes at 600 degrees C, the glass with the photocatalyst film whose thickness is 100nm was obtained.

[0033] Next, the following approach estimated the traverse-proof nature of the obtained glass with the photocatalyst film. It is JIS to a wear cloth. L The broadcloth cloth and sticking-by-pressure area according to 0803 are set to 2 6.25cm, The 0.1kg/cm2 load was added, it slid 1,000 times by part for sliding rate 30 round-trip/, and 10cm of sliding length, this photocatalyst film obtained when the traverse-proof sex test which evaluates membranous adhesion by the existence of exfoliation of the film and existence to which the remarkable film gets damaged was carried out did not have film exfoliation, and it was the film that there is also no blemish and very firm.

[0034] Furthermore, the following approach estimated the photocatalyst activity of the photocatalyst film. Adhere an oleic acid content acetone solution to the photocatalyst film surface of glass with the photocatalyst film 1% of the weight at homogeneity, form dirt artificially, and make the black light (floor line15 made from the NIPPO electrical and electric equipment BLB) into the light source at this. It irradiated for 24 hours and the photocatalyst activity of the photocatalyst film was evaluated more for the ultraviolet rays adjusted to 1.5 mW/cm2 (365nm) with the ultraviolet ray intensity meter (UVPZmade from eye graphics- 2) to measure the decomposition of 4 hours or oleic acid by the photocatalysis by change of the contact angle of water. Consequently, 91 to 4 before the contact angle of water irradiating hours after it was set to 7, 24 more hours after was set to 2, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0035] In addition, the result of an optical activity trial and the traverse-proof sex test is shown in Table 1. (O mark) of the column of evaluation of the optical activity in Table 1, evaluation of traverse-proof nature, and comprehensive evaluation shows a very good result, (O mark) shows a good result and (x mark) shows a rejected result. In addition, the same approach as the above also estimated the traverse-proof nature and photocatalyst activity in the example and the example of a comparison which are shown below.

[0036]

[Example 2] Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — it carried out like the example 1 except having set colloidal silica to 70:30:0:0 (mol %). Glass with the photocatalyst film of 93nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0037] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 90 to 4 before the contact angle of water irradiating hours after it was set to 5, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0038]

[Example 3] It carried out like the example 2 except having used for the base material soda lime glass of 2mm of board thickness which has not prepared the silica film as a substrate layer instead of soda lime glass with the silica film. Glass with the photocatalyst film of 90nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0039] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 71 to 4 before the contact angle of water irradiating hours after it was set to 9, 24 more hours after was set to 4, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0040]

[Example 4] It carried out like the example 1 using the colloidal silica (IPA-ST-S, product made from the Nissan chemistry) as a sol of the particle which the reaction ended instead of the titanium oxide particle as a particle which the reaction ended except having set Ti alkoxide:silica sol:colloidal silica to 90:0:10 (mol %). Glass with the photocatalyst film of 101nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0041] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 84 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0042]

[Example 5] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 4 except having set colloidal silica to 70:0:30 (mol %). Glass with the photocatalyst film of 97nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0043] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 73 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0044]

[Example 6] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 4 except having set colloidal silica to 50:0:50 (mol %). Glass with the photocatalyst film of 89nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0045] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 60 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0046]

[Example 7] It carried out like the example 1 using the silica sol (the COL coat P, made in a COL coat) compounded from hydrolysis and the polycondensation of a silica compound as a source of silicon oxide except having set Ti alkoxide:titanium oxide particle:silica sol:colloidal silica to 40:40:20:0 (mol %). Glass with the photocatalyst film of 83nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0047] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 70 to 4 before the contact angle of water irradiating hours after it was set to 3, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst

film.
[0048]
[Example 8] Colloidal silica (IPA-ST-S, product made from the Nissan chemistry) was used instead of the titanium oxide particle as a particle which the reaction ended, and it carried out like the example 7 except having set chlorine content Ti alkoxide:titanium oxide particle:silica sol:colloidal silica to 40:0:20:20 (mol %). Glass with the photocatalyst film of 81nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0049] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 42 to 4 before the contact angle of water irradiating hours after it was set to 6, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0050]
[Example 9] The silica sol solution was applied to soda lime glass, and it carried out like the example 8 except having used as the base material what was dried at 150 degrees C.
[0051] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 43 to 4 before the contact angle of water irradiating hours after it was set to 10, and has checked having photocatalyst activity with this expensive glass with the photocatalyst film.
[0052]
[Example 10] A silica sol (COL coat P), a titanium oxide sol (ATORON NTi-500, Nippon Soda make), and ethanol were used on the soda lime glass base material, it carried out like the example 8 by oxide conversion except [ % of / 2= 10:90 mol of TiO2:SiO(s) ] having prepared the substrate film of a presentation, and glass with the photocatalyst film was obtained.
[0053] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 45 to 4 before the contact angle of water irradiating hours after it was set to 10, and has checked having photocatalyst activity with this expensive glass with the photocatalyst film.
[0054]
[Example 11] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 except having set colloidal silica to 70:10:20 (mol %). Glass with the photocatalyst film of 98nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0055] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 50 to 4 before the contact angle of water irradiating hours after it was set to 6, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0056]
[Example 12] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 8 except having made colloidal silica into 45:35:20- mol %. Glass with the photocatalyst film of 100nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0057] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 41 to 4 before the contact angle of water irradiating hours after it was set to 3, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film. Moreover, in order to observe the surface irregularity of this printing film, this ink was printed on soda lime glass, and the sample which heat-treated similarly was produced. 2-micrometer scan around of this sample front face was carried out in the AFM mode (atomic force microscope) of a scan mold probe microscope (SPI3700 made from the SEIKO electronic industry), and the surface type-like condition was observed. As for Sratio which shows what time surface area increased with the irregularity of a sample compared with the flat flat surface theoretically, the value of 1.050 was acquired. Moreover, when the value of about 4.9nm was acquired and average side granularity Ra added colloidal silica compared with the below-mentioned example 1 of a comparison, it checked that surface area (surface irregularity) had become large.
[0058]
[Example 13] It carried out like the example 12 except having used for the base material soda lime glass of 2mm of board thickness which has not prepared the silica film as a substrate layer instead of soda lime glass with the silica film. Glass with the photocatalyst film of 101nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0059] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 41 to 4 before the contact angle of water irradiating hours after it was set to 3, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0060]
[Example 14] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 8 except having set colloidal silica to 10:80:10 (mol %). Glass with the photocatalyst film of 98nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0061] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 24 to 4 before the contact angle of water irradiating hours after it was set to 10, 24 more hours after was set to 5, and has checked having photocatalyst activity with this expensive glass with the photocatalyst film.
[0062]
[The example 1 of a comparison] Not using the colloidal silica which is the particle which the reaction ended, it carried out like the example 8 except having set the Ti alkoxide:silica sol:colloidal silica in ink to 45:55:0 (mol %). Glass with the photocatalyst film of 96nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0063] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 45 to 4 before the contact angle of water irradiating hours after it was set to 25, and 24 more hours after was set to 7, and the reduction in a contact angle was not what was excellent especially although it saw. Moreover, in order to observe the surface irregularity of this printing film, this ink was printed on soda lime glass, and the sample which heat-treated similarly was produced. The surface type-like condition was observed for this sample front face by the same approach as an example 5. As for 1.001 and average side granularity Ra, the value of about 1.0nm was acquired, and a result and Sratio checked that this thin film was almost a flat.
[0064]
[The example 2 of a comparison] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 of a comparison except

having set colloidal silica to 75:25:0 (mol %). Glass with the photocatalyst film of 100nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0065] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 66 to 4 before the contact angle of water irradiating hours after it was set to 32, and 24 more hours after was set to 6, and the reduction in a contact angle was not what was excellent especially although it saw.
[0066]
[The example 3 of a comparison] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 of a comparison except having set colloidal silica to 31:69:0 (mol %). Glass with the photocatalyst film of 103nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0067] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 41 to 4 before the contact angle of water irradiating hours after it was set to 29, and 24 more hours after was set to 12, and the reduction in a contact angle was not what was excellent especially although it saw.
[0068]
[The example 4 of a comparison] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 of a comparison except having set colloidal silica to 10:90:0 (mol %). Glass with the photocatalyst film of 97nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0069] As a result of the traverse-proof sex test, this obtained thin film was very firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 30 to 4 before the contact angle of water irradiating hours after it was set to 13, and 24 more hours after was set to 9, and the reduction in a contact angle was not what was excellent especially although it saw.
[0070]
[The example 5 of a comparison] Not using Ti alkoxide, it carried out like the example 7 except having set the Ti alkoxide:titanium oxide particle:silica sol:colloidal silica in ink to 0:10:90:0 (mol %). Exfoliation was seen very easily by this obtained thin film as a result of the traverse-proof sex test.
[0071]
[The example 6 of a comparison] Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — it carried out like the example 5 of a comparison except having set colloidal silica to 0:50:50:0 (mol %). Exfoliation was seen very easily by this obtained thin film as a result of the traverse-proof sex test.
[0072]
[The example 7 of a comparison] Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — it carried out like the example 5 of a comparison except having set colloidal silica to 0:90:10:0 (mol %). Exfoliation was seen very easily by this obtained thin film as a result of the traverse-proof sex test.
[0073]
[The example 8 of a comparison] The increase of the content of the titanium-oxide particle which the reaction ended, the Ti alkoxide:titanium-oxide particle:silica sol in ink: It carried out like the example 1 except having set colloidal silica to 30:70:0:0 (mol %). Glass with the photocatalyst film of 71nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0074] The blemish in which this obtained thin film was weak and remarkable was seen as a result of the traverse-proof sex test. As a result of evaluating photocatalyst activity, 72 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0075]
[The example 9 of a comparison] The increase of the content of colloidal silica, the Ti alkoxide:silica sol in ink: It carried out like the example 4 except having set colloidal silica to 30:0:70 (mol %). Glass with the photocatalyst film of 78nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0076] The blemish in which this obtained thin film was weak and remarkable was seen as a result of the traverse-proof sex test. As a result of evaluating photocatalyst activity, 40 to 4 before the contact angle of water irradiating hours after it was set to 1, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0077]
[Table 1]

| | インキ主成分組成(モル%) | | | | | 光触媒活性(°) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| サンプルNo. | Tiアルコキシド | Ti微粒子 | シリカゲル | コロイダルシリカ | 下地層 | 照射前 | 4時間 | 24時間 | 評価 | 耐トラバース性 | 総合評価 |
| 実施例 1 | 90 | 10 | 0 | 0 | SiO2 | 91 | 7 | 2 | ◎ | ◎ | ◎ |
| 実施例 2 | 70 | 30 | 0 | 0 | SiO2 | 90 | 5 | <1 | ◎ | ◎ | ◎ |
| 実施例 3 | 70 | 30 | 0 | 0 | − | 71 | 9 | 4 | ◎ | ◎ | ◎ |
| 実施例 4 | 90 | 0 | 0 | 10 | SiO2 | 84 | 2 | <1 | ◎ | ◎ | ◎ |
| 実施例 5 | 70 | 0 | 0 | 30 | SiO2 | 73 | 2 | 1 | ◎ | ◎ | ◎ |
| 実施例 6 | 50 | 0 | 0 | 50 | SiO2 | 60 | 2 | 1 | ◎ | ◎ | ◎ |
| 実施例 7 | 40 | 40 | 20 | 0 | SiO2 | 70 | 3 | 1 | ◎ | ◎ | ◎ |
| 実施例 8 | 60 | 0 | 20 | 20 | SiO2 | 42 | 6 | − | ◎ | ◎ | ◎ |
| 実施例 9 | 60 | 0 | 20 | 20 | SiO2 | 43 | 10 | − | ○ | ◎ | ○ |
| 実施例10 | 60 | 0 | 20 | 20 | TiO2-SiO2 | 45 | 10 | − | ○ | ◎ | ○ |
| 実施例11 | 70 | 0 | 10 | 20 | SiO2 | 50 | 6 | − | ◎ | ◎ | ◎ |
| 実施例12 | 45 | 0 | 35 | 20 | SiO2 | 41 | 3 | <1 | ◎ | ◎ | ◎ |
| 実施例13 | 45 | 0 | 35 | 20 | − | 41 | 3 | <1 | ◎ | ◎ | ◎ |
| 実施例14 | 10 | 0 | 80 | 10 | SiO2 | 24 | 10 | 5 | ○ | ◎ | ○ |
| 比較例 1 | 45 | 0 | 55 | 0 | SiO2 | 45 | 25 | 7 | × | ◎ | × |
| 比較例 2 | 75 | 0 | 25 | 0 | SiO2 | 66 | 32 | 6 | × | ◎ | × |
| 比較例 3 | 31 | 0 | 69 | 0 | SiO2 | 41 | 29 | 12 | × | ◎ | × |
| 比較例 4 | 10 | 0 | 90 | 0 | SiO2 | 30 | 13 | 9 | × | ◎ | × |
| 比較例 5 | 0 | 10 | 90 | 0 | SiO2 | − | − | − | − | × | × |
| 比較例 6 | 0 | 50 | 50 | 0 | SiO2 | − | − | − | − | × | × |
| 比較例 7 | 0 | 90 | 10 | 0 | SiO2 | − | − | − | − | × | × |
| 比較例 8 | 30 | 70 | 0 | 0 | SiO2 | 72 | 2 | 1 | ◎ | × | × |
| 比較例 9 | 30 | 0 | 0 | 70 | SiO2 | 40 | 1 | <1 | ◎ | × | × |

[0078]
[Effect of the Invention] Since the ink for photocatalyst film formation of this invention makes the oxide particle which the reaction ended have contained, while its ink is very stable, the photocatalyst film produced using the ink for photocatalyst film formation of this invention while own pot life of ink became long and excelling as ink of print processes, such as screen-stencil, -- the dip coating method of the other membrane formation approaches, the roll coat method, a spin coat method, etc. -- comparing -- photocatalyst activity and abrasion resistance -- inferiority -- there is nothing -- low cost -- high -- the outstanding durability thing is obtained.

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[Translation done.]

## TECHNICAL FIELD

[Industrial Application] This invention relates to the formation approach of the ink for photocatalyst film formation at the time of printing further the glass goods of various kinds of fields, such as sheet glass for construction building materials, such as sheet glass for cars, such as a windowpane for automobiles, a windowpane of a building, and glass of a mirror, and the thin film which had a photocatalyst function in front faces, such as ceramics and a metal, by print processes etc. especially, and a photocatalyst.

[Translation done.]

* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

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PRIOR ART

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[Description of the Prior Art] Recently, it applies for many patents aiming at use of effectiveness, such as antifouling property by the oxidative degradation by the photocatalysis of titanium oxide, or the optical induction super-hydrophilic-property reaction, a hydrophilic property, and fog resistance.
[0003] As a coating solution presentation of the photocatalyst film, the application (JP,8-164334,A) about a titania particle distribution solution, the application (JP,8-299789,A) about Ti alkoxide / alcoholic system, etc. are known, for example.
[0004] Moreover, about the example of membrane formation, screen-stenciling the drug solution which WO 96/No. 13327 official report is made to carry out the reaction dissolution of titanium tetra-isopropoxide, ethyl cellulose, and the organic solvent, and is obtained, for example is indicated.

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[Translation done.]

## EFFECT OF THE INVENTION

[Effect of the Invention] Since the ink for photocatalyst film formation of this invention makes the oxide particle which the reaction ended have contained, while its ink is very stable, the photocatalyst film produced using the ink for photocatalyst film formation of this invention while own pot life of ink became long and excelling as ink of print processes, such as screen-stencil, -- the dip coating method of the other membrane formation approaches, the roll coat method, a spin coat method, etc. -- comparing -- photocatalyst activity and abrasion resistance -- inferiority -- there is nothing -- low cost -- high -- the outstanding durability thing is obtained.

[Translation done.]

## TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In the presentation solution of hypoviscosity like a titania particle part water spray solution like the publication to said JP,8-164334,A, or a titania particle distribution alcoholic solution, condensation of phase splitting by sedimentation of a particle and a particle etc. tends to take place, and a solution cannot necessarily call it stability. Moreover, in Ti alkoxide / an alcoholic system like a publication, drug solution concentration tends to change to JP,8-299789,A that a solvent tends to evaporate. moreover, unstable [ change / the description of solutions, such as phase splitting and aggravation of spreading nature, / tend / with moisture absorption and ] — etc. — there is a problem. Moreover, these solutions are hard to be called drug solution suitable for the print processes which not necessarily need viscosity of dozens to hundreds of poise, such as screen printing.
[0006] Moreover, about a presentation WO96 / given in 13327 official reports, since liquid cannot say it as stability and ethyl cellulose is used as a thickener, membranous reinforcement has the problem of being low that the carbon which is the combustion object tends to remain in the film at the time of baking.

[Translation done.]

MEANS

[Means for Solving the Problem] As the raw material which forms the titanium oxide which makes this invention in view of the technical problem which the former requires, and discovers photocatalyst activity, At least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, the content of the oxide particle which is ink which consists of oxide particles which the reaction ended, and this reaction ended — 5–50–mol% of an ink principal component — by containing It is stabilized without the stability of ink improving extremely and also discovering the trouble in various printings etc., and printing film formation can be performed. Moreover, it is the photocatalyst film produced in this ink being equipped with the photocatalyst effectiveness, abrasion resistance, and endurance, and specifying the refractive index of a thin film, and thickness further. Excitation purity is small and a color offers the formation approach of the useful ink for photocatalyst film formation in which what has small near and a small reflection factor is obtained by the neutral color, and the photocatalyst film.
[0008] That is, after carrying out spreading membrane formation on a base material front face by print processes, it sets in the ink for calcinating and carrying out a solidification coat and forming the photocatalyst film, and this invention is hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound. At least one sort in the sol of the formed titanium oxide, and the ink principal component whose content of the oxide particle which oxide particles which the reaction ended were consisted of and this reaction ended is 5–50–mol% of an ink principal component, It is characterized by being ink for photocatalyst film formation which becomes considering viscosity as 10–100poise using the ink accessory constituent which consists of at least one sort in the nitrocellulose as a thickening component and the ethyl carbitol as a solvent, or butyl carbitol.
[0009] Furthermore, this invention is characterized by the solid content in ink being 1 – 2 % of the weight. [0010] Moreover, after this invention carries out spreading membrane formation of said ink on a base material front face by screen–stencil, gravure, or the intaglio–printing method, it is characterized by the content of the titanium oxide in the photocatalyst film calcinated at the temperature of 250–850 degrees C being the formation approach of the 10–100–mol photocatalyst film which is %. [0011] Furthermore, this invention is characterized by forming the substrate layer which prevents the component used as the cause of it being characterized by a base material being glass, and reducing photocatalyst activity, such as alkali in this glass component, invading into the photocatalyst film, or uses as a principal component the oxide to which trespass is reduced. [0012]
[Embodiment of the Invention] The ink which forms the high–performance photocatalyst film of this invention consists of the raw material which forms the titanium oxide which has photocatalyst activity, a raw material which forms metallic oxides other than titanium oxide, and a metallic–oxide raw material which the reaction ended, a thickener and a solvent contain as an accessory constituent of ink further, and a solidification coat can carry out in the film which make dry and calcinate and has a photocatalyst activity operation after carrying out spreading membrane formation of those ink on a base material front face after mixed adjustment.
[0013] As main raw materials of the ink which forms the titanium oxide which discovers photocatalyst activity, it is at least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, and when using the crystalline titanium oxide particle which the reaction ended, this particle also contributes to photocatalyst activity. When the above–mentioned raw material is explained, it is Ti ARUKOKIDO, For example, a titanium methoxide, titanium ethoxide, titanium propoxide, Titanium butoxide, etc. a halogen content Ti alkoxide, etc. can be used. To a halogen content Ti alkoxide and a thing a chlorine content Ti alkoxide it is not necessary to make it hydrolyze by adding water and a catalyst compared with Ti alkoxide which does not contain the other halogen, to add to ink, and to mix with ink the sol which is in a reaction process by this, and there is an advantage the pot life of ink is markedly easy coming to be alike of an advantage. In addition, Ti acetylacetonato which stabilized the above–mentioned Ti alkoxide by the acetylacetone can also be used.
[0014] Moreover, depending on the case, the sols of the titanium oxide formed of hydrolysis and the polycondensation of Ti compound may be hydrolysis and a sol of titanium oxide which was made to carry out a polycondensation and was obtained about Ti compound which consists of a Ti alkoxide or Ti acetylacetonato, and a commercial item is sufficient, for example, TA–10, TA–15 (Nissan Chemical Industries make), ATORON NTi–500 (Nippon Soda make), etc. can be used as a titanium oxide sol of a commercial item. In addition, adding stabilizing agents generally used for these things, such as hexylene glycol, does not interfere other than an acetylacetone for control of these hydrolysis and polycondensation reactions.
[0015] The metallic–oxide particle which the reaction ended can give an operation very remarkable on the stable disposition of ink, and the particle which consists of titanium oxide, silicon oxide, oxidization aluminum, a zirconium dioxide, tin oxide, etc. can be used for it, and it does not limit the shape of the shape of a particle, and a sol etc. especially about those descriptions. in order that, as for these particles either of metallic oxides other than titanium oxide and titanium oxide is sufficient as whose particles which this reaction ended and that may carry out, and may contain both and the reaction ended, a reaction may not progress further in ink — the description of ink — change can be prevented. It is because it does not have film reinforcement and cannot desire improvement in a property by particle addition less than [ 5 mol % ] to an ink principal component, if it is desirable that it is [ 5–50 mol ] % as for the content of a particle and there are than 50–mol %. [ more ] In addition, an ink principal component here shows at least one sort in the sol of the metallic oxide formed [ with at least one sort in the sol of the titanium oxide formed of hydrolysis and the polycondensation of Ti alkoxide, Ti acetylacetonato, and Ti compound, and the oxide particle which the reaction ended ] of hydrolysis and the polycondensation of the metal alkoxide except a titanium metal, metal acetylacetonato, a metal organic–acid salt, and metallic compounds depending on the case. Moreover, these particles have especially the desirable silica particle that is excellent in the particle of titanium oxide which is excellent in a photocatalyst operation, and/or a water retention operation.

[0016] In addition, as a titanium oxide particle, it is ST-01 (product made from the Ishihara techno), for example as a commercial item, Especially since sufficient photocatalyst activity is acquired even if it can use both distributed solutions, such as fine particles, such as SSP-25 (Sakai Chemical Industry make), STS-01 (product made from the Ishihara techno), and CA-62 (Taki Chemical make), the crystal titanium oxide particle which these reactions ended also has a photocatalyst operation with the improvement operation in stability of ink and it calcinates at low temperature, it is desirable. In addition, since the crystal form can discover the photocatalyst activity in which ANATASU excelled the rutile, it is more desirable. As for the content of the titanium oxide in the photocatalyst film, it is desirable that it is [ 10-100 mol ] %, and it is deficient in photocatalyst activity practical less than [ 10 mol % ]. In addition, the value at the time of carrying out the presentation of the formed film to oxide conversion (mol %) is shown in mol % in the text.

[0017] Moreover, about the particle which other reactions ended, colloidal silica IPA-ST (Nissan Chemical Industries make), alumina sol -10 (Nissan Chemical Industries make), an alumina clear sol (Kawaken Fine Chemicals make), etc. can be used as a commercial item. As for especially the particle size of these particles, it is desirable to use a thing about tennm or less in the case of the base material with which a base material is characterized by the transparency of glass etc. Moreover, in order to acquire higher photocatalyst activity, the front face of a photocatalyst is formed in the shape of irregularity, and these particles are effective also in order to increase the surface area.

[0018] Moreover, it is a raw material which forms metallic oxides other than titanium oxide, The metallic-oxide particle which at least one sort and/or reaction of the sol of a metallic oxide which were formed of hydrolysis and the polycondensation of a metal alkoxide, metal acetylacetonato, a metal organic-acid salt, and metallic compounds ended can be used, and these are added by ink for the various object, such as improvement in photocatalyst functions, such as improvement in endurance, such as film reinforcement, chemical resistance, and adhesion, control of a refractive index, and hydrophilic maintenance nature, and control of printing nature.

[0019] As a metal which forms the metallic oxide, Si, Zr, aluminum, B, P, Sn, etc. can be used, and naphthenate, oxy-acetate, a stearate, etc. can be used as a metal alkoxide as the metal acetylacetonato which stabilized said metal alkoxides, such as these methoxides, ethoxide, propoxide, and butoxide, by the acetylacetone, and a metal organic-acid salt.

[0020] About moreover, metallic-oxide sols other than the titanium oxide which a reaction has not ended They are hydrolysis and the metallic-oxide sol which was made to carry out a polycondensation and was obtained about the organic metal compound which consists of a metal alkoxide or metal acetylacetonato. Depending on the case, a commercial item is sufficient. As a silica sol Soe Per Serra (product made from the Daihachi chemical industry), The COL coat P (made in a COL coat), ATORON NSi-500 (Nippon Soda make), etc., As a zirconia sol, NZS-30A (Nissan Chemical Industries make), AZS-A (product made from the NIPPON SHOKUBAI science industry), etc. can use the sol by HAUTO form MS-AL (product made from the Fuji chemistry), and TOKYO OHKA KOGYO etc. as alumina sol. In addition, adding stabilizing agents generally used for these things, such as hexylene glycol, does not interfere other than an acetylacetone for control of these hydrolysis and polycondensation reactions.

[0021] As for the content of the solid content in ink, it is desirable that it is 1.0 - 2.0 % of the weight in oxide conversion further again. At less than 1.0 % of the weight For example, the thickness obtained by one printing etc. becomes thin too much, and printing unevenness becomes easy to be conspicuous. If the appearance of the obtained thin film will become less desirable, a refractive index will not increase to a theoretical value further, a reflection property and a transparency property change and it exceeds 2.0 % of the weight If the thickness obtained by one printing etc. tends to become thick and is set especially to 150nm or more, it will be easy to generate a crack, and moreover, for this reason, it is for thin film reinforcement, such as traverse-proof nature and the Taber abrasiveness reinforcement, also falling. By carrying out to the 1.0 - 2.0 above-mentioned% of the weight, the homogeneous coat which does not have a crack after the last heat treatment is obtained also in the forming-membranes method the thickness immediately after printings, such as screen-stencil, gravure, and intaglio printing, etc. becomes comparatively thick. In addition, when the solid content in ink here calcinates the ink applied on the base material, it remains into the film as a film structure, and they are a titanium oxide raw material, a metallic-oxide raw material except titanium oxide, and the oxide particle that the reaction ended.

[0022] It is because the thickening effectiveness has good flammability, of course compared with ethyl cellulose etc. and there are few residuals of the carbon component for which the membranous appearance and the film reinforcement after baking are reduced, when a nitrocellulose is used as a thickening component added to ink. Moreover [ especially ], it is JISK about grade. More than H7 (H7, H20, H60, H80, H120) has desirable form and viscosity notation of assignment with 6703, and it is because the better thickening effectiveness and printing nature are obtained. In addition, the addition of a thickening component has 5 - 25 desirable % of the weight, and viscosity of ink can be made into 10-100poise suitable for print processes, such as screen-stencil, gravure, and intaglio printing. In less than 10poise, the viscosity of ink is too low for the time of printing, ink tends to spread on the screen version, it is hard to control desiccation of the ink on a version, and good patterning is no longer obtained. Moreover, it is because the carbon of the cinder of a nitrocellulose remains, and the film will color it a yellowish brown color, the homogeneity of a film surface will be spoiled or the printing nature at the time of screen-stencil not only gets remarkably bad, but it will further become easy for mechanical [ membranous ] and chemical durability to fall into the thin film which baking completed eventually, if it exceeds 100poise.

[0023] The lowering of the refractive index of a thin film or endurance moreover obtained can be prevented without spoiling printing nature and the homogeneity of the thin film obtained by adjusting the class of such a nitrocellulose, an addition, and viscosity. In addition, especially as print processes, the ease of carrying out of patterning to screen-stencil is desirable.

[0024] As the solvent which melts a nitrocellulose by independent [ which is added in ink ], Solvents, such as an acetone, methyl acetate, a methyl ethyl ketone, isopropyl acetate, a diethyl ketone, the 2nd butyl acetate, methyl isobutyl ketone, isobutyl acetate, methyl cellosolve, butyl acetate, the 2nd amyl acetate, ethylcellosolve, methyl-cellosolve acetate, methyl lactate, amyl acetate, ethyl lactate, a cyclohexanone, ethylcellosolve acetate, diacetone alcohol, butyl cellosolve, butyl lactate, ethyl carbitol, butyl carbitol, 3-methoxybutanol, and 3-methoxy butyl acetate, can be used. Since especially carbitols cannot evaporate easily, when it uses as a solvent of ink, the ink by which concentration change was stabilized few is obtained. Moreover, solvents, such as aromatic series solvents, such as alcohols, such as the methanol and ethanol which are supplied, propanol, a butanol, ethylene glycol, and hexylene glycol, benzene, toluene, and a xylene, and water, can be added and used for the above-mentioned solvent for the object, such as concentration adjustment, from the source of Ti, or the other sources of a metallic oxide.

[0025] If ethyl carbitol, butyl carbitols, or such mixture are used as a solvent, since rapid desiccation of the ink before printing etc. can be controlled, for example, and the coat after printing etc. can dry at low temperature (about 200 degrees C) comparatively, therefore pot life will be long and a thin film will moreover dry at low temperature comparatively after printing etc. by these further

again, the coat which has a uniform film surface by heat-treatment of terminal temperature is obtained.
[0026] Glass, the ceramics, a metal, etc. can be used for a base material. Moreover, a base material is soda lime glass etc. Use it and Ti alkoxides etc. and the sols other than a crystalline particle are used especially for the source of Ti of ink. Prevent the component used as the cause of reducing photocatalyst activity, such as alkali in a glass component, invading into the photocatalyst film, when forming the photocatalyst film. Or the photocatalyst film with more high photocatalyst activity is ****** by preparing the substrate film which uses as a principal component any one kind of Si, Ti, Zr, aluminum, B, P, and Sn to which trespass is reduced, or two kinds or more of the arbitration of these of oxides. The substrate film of SiO2, TiO2-SiO2, aluminum2O3-SiO2, and aluminum2O3-TiO2-SiO2 is more desirable in respect of photocatalyst activity and endurance especially. What formed membranes by approaches, such as the general membrane formation approach, for example, the dip coating method using a sol gel process, a spin coat method, the roll coat method, etc. and a CVD method, PVD, in addition to the print processes which used ink may be used for membrane formation of the substrate film. Furthermore, in the case of the substrate film containing the organic component immediately after forming membranes using print processes, a sol gel process, etc., heat treatment of 300 degrees C or more is performed once, and the effectiveness which prevents trespass of alkali etc. more becomes high by burning an organic component and considering as the oxide film.
[0027] As for the printing film using this ink, it is desirable to heat-treat below about 250 degrees C at which it is necessary to heat-treat in order to acquire the film reinforcement and photocatalyst activity according to an application, and especially a nitrocellulose burns, as mentioned above about 850 degrees C transferred to a rutile mold with low photocatalyst activity from an anatase.
[0028] Moreover, when the film with which refractive indexes differ like [ when forming the substrate film of a silica on glass and forming the photocatalyst film of a titania on it further ] is formed on a base material, compared with a base material, the excitation purity of a light echo may increase from the difference of the refractive index remarkably. For example, depending on an application which is expected non-colored glass like the windowpane for cars, the increment in this excitation purity may become a problem. It is possible to fall the increment in excitation purity to 5% or less of hardly worried level by adjusting the thickness and the refractive index of the substrate film and the photocatalyst film to this. Moreover, when coloring is rather liked like **** material, it is also possible to emphasize a reflective stimulus color tone by adjusting the thickness and the refractive index of the substrate film and the photocatalyst film similarly, and to raise design nature.
[0029]
[Example 1] The titanium tetrachloride (TiCl4) was used as the start raw material, and when making isopropyl alcohol react to this and compounding Ti-isopropoxide, the solute concentration which is made to end a reaction, with some chlorine (Cl) left, and has the combination presentation of Ti(OC3H7) xCly (x+y=4) compounded about 13% of the weight of Ti alkoxide by oxide (TiO2) conversion.
[0030] The titanium oxide particle (ST-01, product made from the Ishihara techno) which this acid chlorine content Ti alkoxide and a reaction ended as a source of titanium oxide of the photocatalyst film is used. The whole ink adds a nitrocellulose H7 (product made from a die cel) about 16% of the weight as a thickener in the solution which set colloidal silica to 90:10:0:0 (mol %). Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — The solute concentration of this ink for photocatalyst film formation is become 1.6 % of the weight by oxide conversion and needed. Ethyl carbitol was added as a solvent, mixed churning was improved, and it considered as the ink for photocatalyst film formation. In addition, it was 20poise when the viscosity of ink was measured.
[0031] The base material applied to glass the solution which diluted the silica sol (the COL coat P, made in a COL coat) with ethanol to the soda lime glass plate (2mm thickness, clearance) by dipping, and carried out heating baking at 500 degrees C, and the soda lime glass which attached the silica substrate film of 100nm of thickness was used for it.
[0032] next — predetermined — a configuration — patterning — having carried out — 350 — a mesh — Dacron — a screen — a glass plate — a top — carrying — Shore hardness — HS — 61 — a squeegee — using — said — a photocatalyst — the film — formation — ** — ink — this — a silica — the film — with — glass — a base material — a front face — screen-stenciling — a place — homogeneous — beautiful — patterning — carrying out — having had — printing — the film — obtaining — having had . Then, when heat-treatment was performed for 10 minutes at 600 degrees C, the glass with the photocatalyst film whose thickness is 100nm was obtained.
[0033] Next, the following approach estimated the traverse-proof nature of the obtained glass with the photocatalyst film. It is JIS to a wear cloth. L The broadcloth cloth and sticking-by-pressure area according to 0803 are set to 2 6.25cm, The 0.1kg/cm2 load was added, it slid 1,000 times by part for sliding rate 30 round-trip/, and 10cm of sliding length, this photocatalyst film obtained when the traverse-proof sex test which evaluates membranous adhesion by the existence of exfoliation of the film and existence to which the remarkable film gets damaged was carried out did not have film exfoliation, and it was the film that there is also no blemish and very firm.
[0034] Furthermore, the following approach estimated the photocatalyst activity of the photocatalyst film. Adhere an oleic acid content acetone solution to the photocatalyst film surface of glass with the photocatalyst film 1% of the weight at homogeneity, form dirt artificially, and make the black light (floor line15 made from the NIPPO electrical and electric equipment BLB) into the light source at this. It irradiated for 24 hours and the photocatalyst activity of the photocatalyst film was evaluated more for the ultraviolet rays adjusted to 1.5 mW/cm2 (365nm) with the ultraviolet ray intensity meter (UVPZmade from eye graphics- 2) to measure the decomposition of 4 hours or oleic acid by the photocatalysis by change of the contact angle of water. Consequently, 91 to 4 before the contact angle of water irradiating hours after it was set to 7, 24 more hours after was set to 2, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0035] In addition, the result of an optical activity trial and the traverse-proof sex test is shown in a table 1. (O mark) of the column of assessment of the optical activity in a table 1, assessment of traverse-proof nature, and comprehensive assessment shows a very good result, (O mark) shows a good result and (x mark) shows a rejected result. In addition, the same approach as the above also estimated the traverse-proof nature and photocatalyst activity in the example and the example of a comparison which are shown below.
[0036]
[Example 2] Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — it carried out like the example 1 except having set colloidal silica to 70:30:0:0 (mol %). Glass with the photocatalyst film of 93nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0037] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 90 to 4 before the contact angle of water irradiating hours after it was set

to 5, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0038]
[Example 3] It carried out like the example 2 except having used for the base material soda lime glass of 2mm of board thickness which has not prepared the silica film as a substrate layer instead of soda lime glass with the silica film. Glass with the photocatalyst film of 90nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0039] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 71 to 4 before the contact angle of water irradiating hours after it was set to 9, 24 more hours after was set to 4, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0040]
[Example 4] It carried out like the example 1 using the colloidal silica (IPA-ST-S, product made from the Nissan chemistry) as a sol of the particle which the reaction ended instead of the titanium oxide particle as a particle which the reaction ended except having set Ti alkoxide:silica sol:colloidal silica to 90:0:10 (mol %). Glass with the photocatalyst film of 101nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0041] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 84 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0042]
[Example 5] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 4 except having set colloidal silica to 70:0:30 (mol %). Glass with the photocatalyst film of 97nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0043] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 73 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0044]
[Example 6] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 4 except having set colloidal silica to 50:0:50 (mol %). Glass with the photocatalyst film of 89nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0045] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 60 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0046]
[Example 7] It carried out like the example 1 using the silica sol (the COL coat P, made in a COL coat) compounded from hydrolysis and the polycondensation of a silica compound as a source of silicon oxide except having set Ti alkoxide:titanium oxide particle:silica sol:colloidal silica to 40:40:20:0 (mol %). Glass with the photocatalyst film of 83nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0047] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 70 to 4 before the contact angle of water irradiating hours after it was set to 3, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0048]
[Example 8] Colloidal silica (IPA-ST-S, product made from the Nissan chemistry) was used instead of the titanium oxide particle as a particle which the reaction ended, and it carried out like the example 7 except having set chlorine content Ti alkoxide:titanium oxide particle:silica sol:colloidal silica to 40:0:20:20 (mol %). Glass with the photocatalyst film of 81nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0049] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 42 to 4 before the contact angle of water irradiating hours after it was set to 6, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0050]
[Example 9] The silica sol solution was applied to soda lime glass, and it carried out like the example 8 except having used as the base material what was dried at 150 degrees C.
[0051] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 43 to 4 before the contact angle of water irradiating hours after it was set to 10, and has checked having photocatalyst activity with this expensive glass with the photocatalyst film.
[0052]
[Example 10] A silica sol (COL coat P), a titanium oxide sol (ATORON NTi-500, Nippon Soda make), and ethanol were used on the soda lime glass base material, it carried out like the example 8 by oxide conversion except [ % of / 2= 10:90 mol of TiO2:SiO(s) ] having prepared the substrate film of a presentation, and glass with the photocatalyst film was obtained.
[0053] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 45 to 4 before the contact angle of water irradiating hours after it was set to 10, and has checked having photocatalyst activity with this expensive glass with the photocatalyst film.
[0054]
[Example 11] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 except having set colloidal silica to 70:10:20 (mol %). Glass with the photocatalyst film of 98nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0055] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 50 to 4 before the contact angle of water irradiating hours after it was set

to 6, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0056]
[Example 12] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 8 except having made colloidal silica into 45:35:20- mol %. Glass with the photocatalyst film of 100nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0057] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 41 to 4 before the contact angle of water irradiating hours after it was set to 3, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film. Moreover, in order to observe the surface irregularity of this printing film, this ink was printed on soda lime glass, and the sample which heat-treated similarly was produced. 2-micrometer scan around of this sample front face was carried out in the AFM mode (atomic force microscope) of a scan mold probe microscope (SPI3700 made from the SEIKO electronic industry), and the surface type-like condition was observed. As for Sratio which shows what time surface area increased with the irregularity of a sample compared with the flat flat surface theoretically, the value of 1.050 was acquired. Moreover, when the value of about 4.9nm was acquired and average side granularity Ra added colloidal silica compared with the below-mentioned example 1 of a comparison, it checked that surface area (surface irregularity) had become large.
[0058]
[Example 13] It carried out like the example 12 except having used for the base material soda lime glass of 2mm of board thickness which has not prepared the silica film as a substrate layer instead of soda lime glass with the silica film. Glass with the photocatalyst film of 101nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0059] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 41 to 4 before the contact angle of water irradiating hours after it was set to 3, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.
[0060]
[Example 14] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 8 except having set colloidal silica to 10:80:10 (mol %). Glass with the photocatalyst film of 98nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0061] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 24 to 4 before the contact angle of water irradiating hours after it was set to 10, 24 more hours after was set to 5, and has checked having photocatalyst activity with this expensive glass with the photocatalyst film.
[0062]
[The example 1 of a comparison] Not using the colloidal silica which is the particle which the reaction ended, it carried out like the example 8 except having set the Ti alkoxide:silica sol:colloidal silica in ink to 45:55:0 (mol %). Glass with the photocatalyst film of 96nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0063] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 45 to 4 before the contact angle of water irradiating hours after it was set to 25, and 24 more hours after was set to 7, and the reduction in a contact angle was not what was excellent especially although it saw. Moreover, in order to observe the surface irregularity of this printing film, this ink was printed on soda lime glass, and the sample which heat-treated similarly was produced. The surface type-like condition was observed for this sample front face by the same approach as an example 5. As for 1.001 and average side granularity Ra, the value of about 1.0nm was acquired, and a result and Sratio checked that this thin film was almost a flat.
[0064]
[The example 2 of a comparison] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 of a comparison except having set colloidal silica to 75:25:0 (mol %). Glass with the photocatalyst film of 100nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0065] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 66 to 4 before the contact angle of water irradiating hours after it was set to 32, and 24 more hours after was set to 6, and the reduction in a contact angle was not what was excellent especially although it saw.
[0066]
[The example 3 of a comparison] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 of a comparison except having set colloidal silica to 31:69:0 (mol %). Glass with the photocatalyst film of 103nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0067] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 41 to 4 before the contact angle of water irradiating hours after it was set to 29, and 24 more hours after was set to 12, and the reduction in a contact angle was not what was excellent especially although it saw.
[0068]
[The example 4 of a comparison] Ti alkoxide [ in ink ]: — silica sol: — it carried out like the example 1 of a comparison except having set colloidal silica to 10:90:0 (mol %). Glass with the photocatalyst film of 97nm of thickness by which patterning was carried out homogeneously and finely was obtained.
[0069] As a result of the traverse-proof sex test, this obtained thin film was dramatically firm, and exfoliation and a blemish were not seen. As a result of evaluating photocatalyst activity, 30 to 4 before the contact angle of water irradiating hours after it was set to 13, and 24 more hours after was set to 9, and the reduction in a contact angle was not what was excellent especially although it saw.
[0070]
[The example 5 of a comparison] Not using Ti alkoxide, it carried out like the example 7 except having set the Ti alkoxide:titanium oxide particle:silica sol:colloidal silica in ink to 0:10:90:0 (mol %). Exfoliation was seen very easily by this obtained thin film as a result of the traverse-proof sex test.
[0071]

[The example 6 of a comparison] Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — it carried out like the example 5 of a comparison except having set colloidal silica to 0:50:50:0 (mol %). Exfoliation was seen very easily by this obtained thin film as a result of the traverse-proof sex test.

[0072]

[The example 7 of a comparison] Ti alkoxide [ in ink ]: — titanium oxide particle: — silica sol: — it carried out like the example 5 of a comparison except having set colloidal silica to 0:90:10:0 (mol %). Exfoliation was seen very easily by this obtained thin film as a result of the traverse-proof sex test.

[0073]

[The example 8 of a comparison] The increase of the content of the titanium-oxide particle which the reaction ended, the Ti alkoxide:titanium-oxide particle:silica sol in ink: It carried out like the example 1 except having set colloidal silica to 30:70:0:0 (mol %). Glass with the photocatalyst film of 71nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0074] The blemish in which this obtained thin film was weak and remarkable was seen as a result of the traverse-proof sex test. As a result of evaluating photocatalyst activity, 72 to 4 before the contact angle of water irradiating hours after it was set to 2, 24 more hours after was set to 1, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0075]

[The example 9 of a comparison] The increase of the content of colloidal silica, the Ti alkoxide:silica sol in ink: It carried out like the example 4 except having set colloidal silica to 30:0:70 (mol %). Glass with the photocatalyst film of 78nm of thickness by which patterning was carried out homogeneously and finely was obtained.

[0076] The blemish in which this obtained thin film was weak and remarkable was seen as a result of the traverse-proof sex test. As a result of evaluating photocatalyst activity, 40 to 4 before the contact angle of water irradiating hours after it was set to 1, 24 more hours after became one or less, and has checked having photocatalyst activity with this very expensive glass with the photocatalyst film.

[0077]

[A table 1]

| | インキ主成分組成(モル%) | | | | | 光触媒活性(°) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| サンプルNo. | Tiアルコキシド | Ti微粒子 | シリカゾル | コロイダルシリカ | 下地層 | 照射前 | 4時間 | 24時間 | 評価 | 耐トラバース性 | 総合評価 |
| 実施例 1 | 90 | 10 | 0 | 0 | SiO2 | 91 | 7 | 2 | ◎ | ◎ | ◎ |
| 実施例 2 | 70 | 30 | 0 | 0 | SiO2 | 90 | 5 | <1 | ◎ | ◎ | ◎ |
| 実施例 3 | 70 | 30 | 0 | 0 | — | 71 | 9 | 4 | ◎ | ◎ | ◎ |
| 実施例 4 | 90 | 0 | 0 | 10 | SiO2 | 84 | 2 | <1 | ◎ | ◎ | ◎ |
| 実施例 5 | 70 | 0 | 0 | 30 | SiO2 | 73 | 2 | 1 | ◎ | ◎ | ◎ |
| 実施例 6 | 50 | 0 | 0 | 50 | SiO2 | 60 | 2 | 1 | ◎ | ◎ | ◎ |
| 実施例 7 | 40 | 40 | 20 | 0 | SiO2 | 70 | 3 | 1 | ◎ | ◎ | ◎ |
| 実施例 8 | 60 | 0 | 20 | 20 | SiO2 | 42 | 6 | — | ◎ | ◎ | ◎ |
| 実施例 9 | 60 | 0 | 20 | 20 | SiO2 | 43 | 10 | — | ○ | ◎ | ○ |
| 実施例10 | 60 | 0 | 20 | 20 | TiO2-SiO2 | 45 | 10 | — | ○ | ◎ | ○ |
| 実施例11 | 70 | 0 | 10 | 20 | SiO2 | 50 | 6 | — | ◎ | ◎ | ◎ |
| 実施例12 | 45 | 0 | 35 | 20 | SiO2 | 41 | 3 | <1 | ◎ | ◎ | ◎ |
| 実施例13 | 45 | 0 | 35 | 20 | — | 41 | 3 | <1 | ◎ | ◎ | ◎ |
| 実施例14 | 10 | 0 | 80 | 10 | SiO2 | 24 | 10 | 5 | ○ | ◎ | ○ |
| 比較例 1 | 45 | 0 | 55 | 0 | SiO2 | 45 | 25 | 7 | × | ◎ | × |
| 比較例 2 | 75 | 0 | 25 | 0 | SiO2 | 66 | 32 | 6 | × | ◎ | × |
| 比較例 3 | 31 | 0 | 69 | 0 | SiO2 | 41 | 29 | 12 | × | ◎ | × |
| 比較例 4 | 10 | 0 | 90 | 0 | SiO2 | 30 | 13 | 9 | × | ◎ | × |
| 比較例 5 | 0 | 10 | 90 | 0 | SiO2 | — | — | — | — | × | × |
| 比較例 6 | 0 | 50 | 50 | 0 | SiO2 | — | — | — | — | × | × |
| 比較例 7 | 0 | 90 | 10 | 0 | SiO2 | — | — | — | — | × | × |
| 比較例 8 | 30 | 70 | 0 | 0 | SiO2 | 72 | 2 | 1 | ◎ | × | × |
| 比較例 9 | 30 | 0 | 0 | 70 | SiO2 | 40 | 1 | <1 | ◎ | × | × |

[Translation done.]

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(54)【発明の名称】光触媒膜形成用インキおよび光触媒膜の形成方法



(57)【特許請求の範囲】

【請求項１】印刷法により基材表面に塗布成膜したのち焼成し固化被覆させて光触媒膜を形成するためのインキにおいて、Ｔｉアルコキシド、Ｔｉアセチルアセトナート、Ｔｉ化合物の加水分解および重縮合により形成された酸化チタンのゾルの内の少なくとも１種と、反応の終結した酸化物微粒子から構成され、該反応の終結した酸化物微粒子の含有量がインキ主成分の５～５０モル％であるインキ主成分と、増粘成分としてのニトロセルロースおよび溶媒としてのエチルカルビトールまたはブチルカルビトールの内の少なくとも１種よりなるインキ副成分とを用い、粘度を１０～１００ポイズとしてなることを特徴とする光触媒膜形成用インキ。

【請求項２】インキ中の固形分は１～２重量％であることを特徴とする請求項１記載の光触媒膜形成用インキ。



【請求項３】請求項１または２記載のインキをスクリーン印刷、グラビア印刷、または凹版印刷法により基材表面に塗布成膜したのち、２５０～８５０℃の温度で焼成する光触媒膜中の酸化チタンの含有量が１０～１００モル％であることを特徴とする光触媒膜の形成方法。

【請求項４】基材がガラスであることを特徴とする請求項３記載の光触媒膜の形成方法。

【請求項５】ガラス成分中のアルカリなどの光触媒活性を低下させる原因となる成分が光触媒膜へ侵入するのを防ぐ、あるいは侵入を低下させる酸化物を主成分とする下地層を形成することを特徴とする請求項４記載の光触媒膜の形成方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、自動車用窓ガラスなど

の車両用板ガラス、ビルの窓ガラス、鏡のガラスなどの建築建材用板ガラスなどの各種の分野のガラス物品、さらにはセラミックス、金属などの表面に、ことに印刷法などによって光触媒機能を持った薄膜を印刷する際の光触媒膜形成用インキおよび光触媒の形成方法に関する。

【０００２】

【従来の技術】最近、酸化チタンの光触媒反応による酸化分解反応や光誘起超親水性反応による防汚性、親水性、防曇性などの効果の利用を目的とした特許が数多く出願されている。

【０００３】その光触媒膜のコーティング溶液組成としては、例えばチタニア微粒子分散溶液に関する出願（特開平８－１６４３３４号公報）、Ｔｉアルコキシド／アルコール系に関する出願（特開平８－２９９７８９号公報）などが知られている。

【０００４】また、成膜例については、例えばＷＯ９６／１３３２７号公報に、チタニウムテトライソプロポキシドとエチルセルロース、有機溶剤を反応溶解させて得られる薬液をスクリーン印刷することが開示されている。

【０００５】

【発明が解決しようとする問題点】前記特開平８－１６４３３４号公報に記載のようなチタニア微粒子分散水溶液やチタニア微粒子分散アルコール溶液のような低粘度の組成溶液においては、微粒子の沈降による分相、微粒子の凝集などが起こりやすく、必ずしも溶液が安定とは言えない。また特開平８－２９９７８９号公報に記載のようなＴｉアルコキシド／アルコール系においては、溶媒が蒸発しやすく薬液濃度が変化しやすい。また吸湿により分相や塗布性の悪化などの溶液の性状が変化しやすく不安定であるなどの問題がある。また、これらの溶液は必ずしもスクリーン印刷法などの数十から数百ポイズの粘度を必要とする印刷法に向いた薬液とは言い難い。

【０００６】またＷＯ９６／１３３２７公報記載の組成については、液が安定とはいえず、また増粘剤としてエチルセルロースを用いているため、焼成時にその燃焼物である炭素が膜中に残留しやすく膜の強度は低いという問題がある。

【０００７】

【問題点を解決するための手段】本発明は、従来のかかる課題に鑑みてなしたものであって、光触媒活性を発現する酸化チタンを形成する原料として、Ｔｉアルコキシド、Ｔｉアセチルアセトナート、Ｔｉ化合物の加水分解および重縮合により形成された酸化チタンのゾルの内の少なくとも１種と、反応の終結した酸化物微粒子から構成されるインキであって、該反応の終結した酸化物微粒子の含有量がインキ主成分の５～５０モル％含有することで、インキの安定性が極めて向上し、各種印刷などでのトラブルも発現することなく安定して印刷膜形成ができ、またこのインキにより作製した光触媒膜は光触媒効果、耐摩耗性、耐久性を備え、さらに薄膜の屈折率、膜厚を規定することで、刺激純度が小さくかつ色はニュートラル色に近く、反射率が小さいものが得られる、有用な光触媒膜形成用インキおよび光触媒膜の形成方法を提供するものである。

【０００８】すなわち、本発明は、印刷法により基材表面に塗布成膜したのち焼成し固化被覆させて光触媒膜を形成するためのインキにおいて、Ｔｉアルコキシド、Ｔｉアセチルアセトナート、Ｔｉ化合物の加水分解および重縮合により形成された酸化チタンのゾルの内の少なくとも１種と、反応の終結した酸化物微粒子から構成され、該反応の終結した酸化物微粒子の含有量がインキ主成分の５～５０モル％であるインキ主成分と、増粘成分としてのニトロセルロースおよび溶媒としてのエチルカルビトールまたはブチルカルビトールの内の少なくとも１種よりなるインキ副成分とを用い、粘度を１０～１００ポイズとしてなる光触媒膜形成用インキであることを特徴とする。

【０００９】さらに、本発明は、インキ中の固形分は１～２重量％であることを特徴とする。

【００１０】また本発明は、前記インキをスクリーン印刷、グラビア印刷、または凹版印刷法により基材表面に塗布成膜したのち、２５０～８５０℃の温度で焼成する光触媒膜中の酸化チタンの含有量が１０～１００モル％である光触媒膜の形成方法であることを特徴とする。

【００１１】さらに、本発明は、基材がガラスであることを特徴とし、また該ガラス成分中のアルカリなどの光触媒活性を低下させる原因となる成分が光触媒膜へ侵入するのを防ぐ、あるいは侵入を低下させる酸化物を主成分とする下地層を形成することを特徴とする。

【００１２】

【発明の実施の形態】本発明の高性能光触媒膜を形成するインキは、光触媒活性を有する酸化チタンを形成する原料と、酸化チタン以外の金属酸化物を形成する原料、反応の終結した金属酸化物原料からなり、さらにインキの副成分として増粘剤および溶媒を含有し、それらのインキを混合調整後、基材表面に塗布成膜したのち、乾燥・焼成させ光触媒活性作用を有する膜を固化被覆することができる。

【００１３】光触媒活性を発現する酸化チタンを形成するインキの主な原料としては、Ｔｉアルコキシド、Ｔｉアセチルアセトナート、Ｔｉ化合物の加水分解および重縮合により形成された酸化チタンのゾルの内の少なくとも１種であり、反応の終結した結晶性酸化チタン微粒子を用いる時はこの微粒子も光触媒活性に寄与する。上記原料について説明すると、Ｔｉアルコキドとしては、例えばチタンメトキシド、チタンエトキシド、チタンプロポキシド、チタンブトキシドなどやハロゲン含有Ｔｉアルコキシドなどを用いることができ、ハロゲン含有Ｔｉアルコキシド、ことに塩素含有Ｔｉアルコキシドは、そ

れ以外のハロゲンを含まないＴｉアルコキシドに比べて水や触媒を加えて加水分解をさせてインキに加える必要がなく、これにより反応過程にあるゾルをインキに混ぜなくても良く、インキのポットライフが格段に良くなる利点がある。なお、上記Ｔｉアルコキシドをアセチルアセトンで安定化したＴｉアセチルアセトナートも用いることができる。

【００１４】また、Ｔｉ化合物の加水分解および重縮合により形成された酸化チタンのゾルとは、ＴｉアルコキシドあるいはＴｉアセチルアセトナートなどからなるＴｉ化合物を加水分解・重縮合させて得た酸化チタンのゾルであり、場合によっては市販品でもよく、例えば市販品の酸化チタンゾルとしては、ＴＡ－１０，ＴＡ－１５（日産化学工業製）、アトロンＮＴｉ－５００（日本曹達製）などを用いることができる。なお、これらの加水分解・重縮合反応の制御のためにアセチルアセトン以外にヘキシレングリコールなど一般にこれらのものに用いられる安定化剤を添加することは差し支えない。

【００１５】反応の終結した金属酸化物微粒子は、インキの安定性向上に極めて顕著な作用を付与し、酸化チタン、酸化ケイ素、酸化アルミ、酸化ジルコニウム、酸化スズなどからなる微粒子を用いることが出来、それらの性状については微粒子状、ゾル状等特に限定するものではない。この反応が終結した微粒子は、酸化チタン、酸化チタン以外の金属酸化物のいずれか一方でも良いし、両者を含んでいてもよく、反応が終結したこれらの微粒子は、インキ中で反応がさらに進むことがないために、インキの性状変化を防ぐことが出来る。微粒子の含有量はインキ主成分に対して５～５０モル％であることが好ましく、５０モル％より多いと膜強度がなく、また５モル％未満では微粒子添加による特性向上が望めないからである。なお、ここでいうインキ主成分とは、Ｔｉアルコキシド、Ｔｉアセチルアセトナート、Ｔｉ化合物の加水分解および重縮合により形成された酸化チタンのゾルの内の少なくとも１種と、反応の終結した酸化物微粒子と、場合によってはチタン金属を除く金属アルコキシド、金属アセチルアセトナート、金属有機酸塩、金属化合物の加水分解および重縮合により形成された金属酸化物のゾルの内の少なくとも１種を示す。また、これらの微粒子は光触媒作用に優れる酸化チタンの微粒子および／または保水作用に優れるシリカ微粒子が特に好ましい。

【００１６】なお、酸化チタン微粒子としては、例えば市販品としてはＳＴ－０１（石原テクノ製）、ＳＳＰ－２５（堺化学工業製）などの粉体、ＳＴＳ－０１（石原テクノ製）、ＣＡ－６２（多木化学製）などの分散溶液の両方を用いることができ、これらの反応が終結した結晶酸化チタン微粒子は、インキの安定性向上作用とともに、光触媒作用もあり、低温で焼成しても充分な光触媒活性が得られるので特に好ましい。なお、その結晶形はルチルよりアナターゼの方が優れた光触媒活性を発現できるのでより好ましい。光触媒膜中の酸化チタンの含有量は１０～１００モル％であることが好ましく、１０モル％未満では、実用的に光触媒活性が乏しい。なお、本文中のモル％とは、成膜された膜の組成を酸化物換算（モル％）にした場合の値を示す。

【００１７】また、その他の反応の終結した微粒子については、市販品として例えばコロイダルシリカＩＰＡ－ＳＴ（日産化学工業製）、アルミナゾル－１０（日産化学工業製）、アルミナクリアゾル（川研ファインケミカル製）等を用いることが出来る。これらの微粒子の粒径は、特に基材がガラスなどの透明性を特徴とする基材の場合には、十数ｎｍ以下のものを用いることが望ましい。また、より高い光触媒活性を得るために光触媒の表面を凹凸状に形成し、その表面積を増加するためにもこれらの微粒子は効果がある。

【００１８】また、酸化チタン以外の金属酸化物を形成する原料としては、金属アルコキシド、金属アセチルアセトナート、金属有機酸塩、金属化合物の加水分解および重縮合により形成された金属酸化物のゾルの少なくとも１種および／または反応が終結した金属酸化物微粒子を用いることができ、これらは膜強度や耐薬品性や密着性などの耐久性の向上、屈折率の制御、親水維持性などの光触媒機能の向上、印刷性の制御など様々な目的でインキに添加される。

【００１９】その金属酸化物を形成する金属としてはＳｉ、Ｚｒ、Ａｌ、Ｂ、Ｐ、Ｓｎなどを用いることができ、金属アルコキシドとしては、これらのメトキシド、エトキシド、プロポキシド、ブトキシドなど、前記金属アルコキシドをアセチルアセトンで安定化した金属アセチルアセトナート、金属有機酸塩としてはナフテン酸塩、オキシ酢酸塩、ステアリン酸塩などを用いることができる。

【００２０】また、反応の終結していない酸化チタン以外の金属酸化物ゾルとは、金属アルコキシドあるいは金属アセチルアセトナートからなる金属有機化合物を加水分解・重縮合させて得た金属酸化物ゾルであり、場合によっては市販品でもよく、例えばシリカゾルとしてはスーパーセラ（大八化学工業製）、コルコートＰ（コルコート製）、アトロンＮＳｉ－５００（日本曹達製）など、ジルコニアゾルとしてはＮＺＳ－３０Ａ（日産化学工業製）、ＡＺＳ－Ａ（日本触媒科学工業製）など、アルミナゾルとしてはハウトフォームＭＳ－ＡＬ（富士化学製）、東京応化工業製のゾル、などを用いることができる。なお、これらの加水分解・重縮合反応の制御のためにアセチルアセトン以外にヘキシレングリコールなど一般にこれらのものに用いられる安定化剤を添加することは差し支えない。

【００２１】さらにまた、インキ中の固形分の含有率は、酸化物換算で１．０～２．０重量％であることが好ま

しく、１．０重量％未満では、例えば一回の印刷などで得られる膜厚が薄くなり過ぎて、印刷むらが目立ち易くなり、得られた薄膜の外観が好ましくなくなり、さらに屈折率が理論値まで上がらなくなり、反射特性や透過特性が変わってしまい、２．０重量％を超えると、一回の印刷などで得られる膜厚が厚くなり易く、特に１５０ｎｍ以上になるとクラックが発生し易いし、しかもこのため、耐トラバース性やテーバー摩耗性強度などの薄膜強度も低下するためであり、上記１．０～２．０重量％にすることで、スクリーン印刷、グラビア印刷、凹版印刷など印刷などの直後の膜厚が比較的厚くなる成膜法においても、最終熱処理後にもクラックのない均質な被膜が得られる。なお、ここでいうインキ中の固形分とは、基材上に塗布したインクを焼成した場合に、膜構成物として膜中に残るものであり、それらは酸化チタン原料、酸化チタンを除く金属酸化物原料、反応の終結した酸化物微粒子である。

【００２２】インキに加える増粘成分としてニトロセルロースを用いると、増粘効果はもちろん、エチルセルロースなどに比べて燃焼性が良く、焼成後の膜の外観や膜強度を低下させる炭素成分の残留が少ないからである。また特にグレードをＪＩＳ　６７０３に指定の品種および粘度記号がＨ７以上（Ｈ７、Ｈ２０、Ｈ６０、Ｈ８０、Ｈ１２０）が好ましく、より良好な増粘効果と、印刷性が得られるからである。なお、増粘成分の添加量は５～２５重量％が好ましく、インキの粘度をスクリーン印刷、グラビア印刷、凹版印刷などの印刷法に適した１０～１００ポイズにすることができる。１０ポイズ未満では印刷時にはインキの粘度が低過ぎて、スクリーン版上でインキが広がり易く、版上でのインキの乾燥を抑制し難く、良好なパターニングが得られなくなる。また１００ポイズを超えるとスクリーン印刷時の印刷性が著しく悪くなるばかりでなく、最終的に焼成が完了した薄膜中にニトロセルロースの燃え残りのカーボンが残留して膜が黄褐色に着色したり、膜面の均質性が損なわれたり、さらに膜の機械的、化学的耐久性が低下したりし易くなるからである。

【００２３】このようなニトロセルロースの種類、添加量、粘度を調整することによって印刷性、得られる薄膜の均質性を損なうことなくしかも得られる薄膜の屈折率や耐久性の低下を防止することができる。なお、印刷法としてはパターニングのし易さから、スクリーン印刷が特に好ましい。

【００２４】インキに添加する単独でニトロセルロースを溶かす溶剤としては、アセトン、酢酸メチル、メチルエチルケトン、イソプロピルアセテート、ジエチルケトン、第２酢酸ブチル、メチルイソブチルケトン、イソブチルアセテート、メチルセロソルブ、酢酸ブチル、第２酢酸アミル、エチルセロソルブ、メチルセロソルブアセテート、乳酸メチル、酢酸アミル、乳酸エチル、シクロヘキサノン、エチルセロソルブアセテート、ジアセトンアルコール、ブチルセロソルブ、乳酸ブチル、エチルカルビトール、ブチルカルビトール、３－メトキシブタノール、３－メトキシブチルアセテートなどの溶剤を用いることができる。特に、カルビトール類は蒸発しにくいことから、インキの溶剤として用いた場合、濃度変化が少なく安定したインキが得られる。またＴｉ源やその他の金属酸化物源から供給される、メタノール、エタノール、プロパノール、ブタノール、エチレングリコール、ヘキシレングリコールなどのアルコール類、ベンゼン、トルエン、キシレンなどの芳香族溶媒、水などの溶媒を濃度調整などの目的で上記溶剤に加えて用いることができる。

【００２５】さらにまた、溶媒としてエチルカルビトールもしくはブチルカルビトールあるいはこれらの混合物を用いると、例えば印刷などの前のインキの急激な乾燥を抑制でき、かつ印刷などの後被膜が比較的低温（約２００℃程度）で乾燥でき、したがってこれらによって、ポットライフが長くしかも印刷などの後には比較的低温で薄膜が乾燥するため、最終温度の加熱処理によって均一な膜面をもつ被膜が得られる。

【００２６】基材には、ガラスやセラミックス、金属などを用いることができる。また基材がソーダライムガラスなどを使用し、特にインキのＴｉ源に結晶性微粒子以外のＴｉアルコキシドなどやゾルを用いて、光触媒膜を形成する場合、ガラス成分中のアルカリなどの光触媒活性を低下させる原因となる成分が光触媒膜へ侵入するのを防ぐ、あるいは侵入を低下させるＳｉ、Ｔｉ、Ｚｒ、Ａｌ、Ｂ、Ｐ、Ｓｎのいずれか１種類もしくはこれらのうちの任意の２種類以上の酸化物を主成分とする下地膜を設けることで、より光触媒活性が高い光触媒膜が得らる。特に$SiO_2$、$TiO_2-SiO_2$、$Al_2O_3-SiO_2$、$Al_2O_3-TiO_2-SiO_2$の下地膜が光触媒活性、耐久性の点でより望ましい。下地膜の成膜はインキを用いた印刷法など以外に、一般的な成膜方法、例えばゾルゲル法を用いたディップコート法、スピンコート法、ロールコート法などやＣＶＤ法、ＰＶＤ法などの方法で成膜したものでも良い。さらに、印刷法や、ゾルゲル法などを用いて成膜した直後の有機成分を含む下地膜の場合、一度３００℃以上の熱処理を行い、有機成分を燃焼させて酸化物膜とすることで、よりアルカリなどの侵入を防ぐ効果が高くなる。

【００２７】該インキを用いた印刷膜は、用途に応じた膜強度と光触媒活性を得るために熱処理する必要があり、特にニトロセルロースが燃焼する約２５０℃以上から、アナターゼ型から光触媒活性が低いルチル型に転移する約８５０℃以下で熱処理することが望ましい。

【００２８】また、ガラス上にシリカの下地膜を形成し、さらにその上にチタニアの光触媒膜を形成する時のように屈折率が異なる膜を基材上に形成した場合、その

屈折率の差から、基材に比べて著しく可視光反射の刺激純度が増加する場合がある。例えば車両用窓ガラスのように無着色のガラスが望まれるような用途によってはこの刺激純度の増加が問題になる場合がある。これに対しては、下地膜と光触媒膜の膜厚と屈折率を調整することで刺激純度の増加を５％以下のほとんど気にならないレベルまで低下することが可能である。また建装材のように着色がむしろ好まれる場合には、同様に下地膜と光触媒膜の膜厚と屈折率を調整することで反射刺激色調を強調し意匠性を高めることも可能である。

【００２９】

【実施例１】四塩化チタン（$TiCl_4$）を出発原料とし、これにイソプロピルアルコールを反応させてＴｉ－イソプロポキシドを合成する際、塩素（Ｃｌ）の一部を残したまま反応を終了させて$Ti(OC_3H_7)_xCl_y$（ｘ＋ｙ＝４）の化合組成をもつ溶質濃度が酸化物（$TiO_2$）換算で約１３重量％のＴｉアルコキシドを合成した。

【００３０】光触媒膜の酸化チタン源としてこの酸性の塩素含有Ｔｉアルコキシドと反応の終結した酸化チタン微粒子（ＳＴ－０１、石原テクノ製）を用い、インキ中のＴｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを９０：１０：０：０（モル％）とした溶液に増粘剤としてニトロセルロースＨ７（ダイセル製）をインキ全体の約１６重量％添加し、該光触媒膜形成用インキの溶質濃度が酸化物換算で１.６重量％となるよう、エチルカルビトールを溶媒として添加し、良く混合撹拌し光触媒膜形成用インキとした。なお、インキの粘度を測ったところ２０ポイズであった。

【００３１】基材は、ソーダライムガラス板（２ｍｍ厚、クリアー）にシリカゾル（コルコートＰ、コルコート製）をエタノールで希釈した溶液をディッピングでガラスに塗布し５００℃で加熱焼成し、膜厚１００ｎｍのシリカ下地膜を付けたソーダライムガラスを用いた。

【００３２】次に、所定形状にパターニングした３５０メッシュのテトロンスクリーンをガラス板上にのせ、ショアー硬度ＨＳ６１のスキージーを用いて前記光触媒膜形成用インキで該シリカ膜付きガラス基材表面にスクリーン印刷しところ、均質できれいにパターニングされた印刷膜が得られた。その後、６００℃で１０分間加熱処理を行ったところ、膜厚が１００ｎｍの光触媒膜付きガラスが得られた。

【００３３】次に、下記の方法により、得られた光触媒膜付きガラスの耐トラバース性を評価した。摩耗布にＪＩＳ　Ｌ　０８０３に準じたブロード布、圧着面積を６.２５ｃｍ²として、０.１ｋｇ／ｃｍ²の荷重を加え、摺動速度３０往復／分、摺動長１０ｃｍで１,０００回摺動し、膜の剥離の有無と著しい膜の傷付きの有無で膜の密着性を評価する耐トラバース性試験をしたところ、得られた該光触媒膜は膜剥離がなく、傷も皆無で非常に強固な膜であった。

【００３４】さらに、下記の方法により光触媒膜の光触媒活性を評価した。光触媒膜付きガラスの光触媒膜面に１重量％オレイン酸含有アセトン溶液を均一に付着し人工的に汚れを形成し、これにブラックライト（ニッポ電気製ＦＬ１５ＢＬＢ）を光源として紫外線強度計（アイグラフィックス製ＵＶＰＺ－２）で１.５ｍＷ／ｃｍ²（３６５ｎｍ）に調節した紫外線を４時間または２４時間照射し、光触媒反応によるオレイン酸の分解を水の接触角の変化で測定するにより光触媒膜の光触媒活性を評価した。その結果、水の接触角が照射前の９１から４時間後には７になり、さらに２４時間後には２になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００３５】なお、表１に光活性試験および耐トラバース性試験の結果を示す。表１における光活性の評価、耐トラバース性の評価および総合評価の欄の（◎印）は極めて良好な結果を示したものであり、（○印）は良好な結果を示したものであり、（×印）は不合格の結果を示したものである。なお、以下示す実施例および比較例における耐トラバース性および光触媒活性も上記と同じ方法で評価した。

【００３６】

【実施例２】インキ中のＴｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを７０：３０：０：０（モル％）とした以外は実施例１と同様に行った。均質できれいにパターニングされた膜厚９３ｎｍの光触媒膜付きガラスが得られた。

【００３７】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の９０から４時間後には５になり、さらに２４時間後には１以下になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００３８】

【実施例３】シリカ膜付きソーダライムガラスの代わりに、下地層としてのシリカ膜を設けていない板厚２ｍｍのソーダライムガラスを基材に用いた以外は実施例２と同様に行った。均質できれいにパターニングされた膜厚９０ｎｍの光触媒膜付きガラスが得られた。

【００３９】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の７１から４時間後には９になり、さらに２４時間後には４になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００４０】

【実施例４】反応の終結した微粒子として酸化チタン微粒子の代わりに反応の終結した微粒子のゾルとしてのコロイダルシリカ（ＩＰＡ－ＳＴ－Ｓ、日産化学製）を用

い、Ｔｉアルコキシド：シリカゾル：コロイダルシリカを９０：０：１０（モル％）とした以外は実施例１と同様に行った。均質できれいにパターニングされた膜厚１０１ｎｍの光触媒膜付きガラスが得られた。

【００４１】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の８４から４時間後には２になり、さらに２４時間後には１以下になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００４２】

【実施例５】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを７０：０：３０（モル％）とした以外は実施例４と同様に行った。均質できれいにパターニングされた膜厚９７ｎｍの光触媒膜付きガラスが得られた。

【００４３】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の７３から４時間後には２になり、さらに２４時間後には１になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００４４】

【実施例６】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを５０：０：５０（モル％）とした以外は実施例４と同様に行った。均質できれいにパターニングされた膜厚８９ｎｍの光触媒膜付きガラスが得られた。

【００４５】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の６０から４時間後には２になり、さらに２４時間後には１になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００４６】

【実施例７】酸化ケイ素源としてシリカ化合物の加水分解・重縮合から合成されたシリカゾル（コルコートＰ、コルコート製）を用い、Ｔｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを４０：４０：２０：０（モル％）とした以外は実施例１と同様に行った。均質できれいにパターニングされた膜厚８３ｎｍの光触媒膜付きガラスが得られた。

【００４７】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の７０から４時間後には３になり、さらに２４時間後には１になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００４８】

【実施例８】反応の終結した微粒子として酸化チタン微粒子の代わりにコロイダルシリカ（ＩＰＡ－ＳＴ－Ｓ、日産化学製）を用い、塩素含有Ｔｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを４０：０：２０：２０（モル％）とした以外は実施例７と同様に行った。均質できれいにパターニングされた膜厚８１ｎｍの光触媒膜付きガラスが得られた。

【００４９】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４２から４時間後には６になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００５０】

【実施例９】シリカゾル溶液をソーダライムガラスに塗布し、１５０℃で乾燥したものを基材とした以外は実施例８と同様に行った。

【００５１】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４３から４時間後には１０になり、該光触媒膜付きガラスが高い光触媒活性を有することが確認できた。

【００５２】

【実施例１０】ソーダライムガラス基材上にシリカゾル（コルコートＰ）と酸化チタンゾル（アトロンＮＴｉ－５００、日本曹達製）とエタノールを用いて酸化物換算で$TiO_2$：$SiO_2$＝１０：９０モル％の組成の下地膜を設けた以外は実施例８と同様に行い光触媒膜付きガラスを得た。

【００５３】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４５から４時間後には１０になり、該光触媒膜付きガラスが高い光触媒活性を有することが確認できた。

【００５４】

【実施例１１】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを７０：１０：２０（モル％）とした以外は実施例１と同様に行った。均質できれいにパターニングされた膜厚９８ｎｍの光触媒膜付きガラスが得られた。

【００５５】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の５０から４時間後には６になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００５６】

【実施例１２】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを４５：３５：２０モル％とした以外は、実施例８と同様に行った。均質できれいにパターニングされた膜厚１００ｎｍの光触媒膜付きガラスが得られた。

【００５７】耐トラバース性試験の結果、得られた該薄

膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４１から４時間後には３になり、さらに２４時間後には１以下になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。またこの印刷膜の表面凹凸を観察するために、このインキをソーダライムガラス上に印刷し、同様に熱処理を行った試料を作製した。この試料表面を走査型プローブ顕微鏡（セイコー電子工業製ＳＰＩ３７００）のＡＦＭモード（原子間力顕微鏡）で２μｍ四方スキャンし、表面形状状態を観察した。理論的にフラットな平面に比べて、試料の凹凸により何倍表面積が増えたかを示すＳratioは１．０５０の値が得られた。また平均面粗さＲａは約４．９ｎｍの値が得られ、後述の比較例１に比べてコロイダルシリカを添加したことにより表面積（表面の凹凸）が大きくなったことを確認した。

【００５８】

【実施例１３】シリカ膜付きソーダライムガラスの代わりに、下地層としてのシリカ膜を設けていない板厚２ｍｍのソーダライムガラスを基材に用いた以外は実施例１２と同様に行った。均質できれいにパターニングされた膜厚１０１ｎｍの光触媒膜付きガラスが得られた。

【００５９】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４１から４時間後には３になり、さらに２４時間後には１以下になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００６０】

【実施例１４】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを１０：８０：１０（モル％）とした以外は実施例８と同様に行った。均質できれいにパターニングされた膜厚９８ｎｍの光触媒膜付きガラスが得られた。

【００６１】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の２４から４時間後には１０になり、さらに２４時間後には５になり、該光触媒膜付きガラスが高い光触媒活性を有することが確認できた。

【００６２】

【比較例１】反応の終結した微粒子であるコロイダルシリカを用いず、インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを４５：５５：０（モル％）とした以外は実施例８と同様に行った。均質できれいにパターニングされた膜厚９６ｎｍの光触媒膜付きガラスが得られた。

【００６３】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４５から４時間後には２５になりさらに２４時間後には７になり、接触角の減少はみられたが特に優れたものではなかった。またこの印刷膜の表面凹凸を観察するために、このインキをソーダライムガラス上に印刷し、同様に熱処理を行った試料を作製した。この試料表面を実施例５と同様の方法で表面形状状態を観察した。結果、Ｓratioは１．００１、平均面粗さＲａは約１．０ｎｍの値が得られ、該薄膜がほとんどフラットであることを確認した。

【００６４】

【比較例２】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを７５：２５：０（モル％）とした以外は比較例１と同様に行った。均質できれいにパターニングされた膜厚１００ｎｍの光触媒膜付きガラスが得られた。

【００６５】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の６６から４時間後には３２になりさらに２４時間後には６になり、接触角の減少はみられたが特に優れたものではなかった。

【００６６】

【比較例３】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを３１：６９：０（モル％）とした以外は比較例１と同様に行った。均質できれいにパターニングされた膜厚１０３ｎｍの光触媒膜付きガラスが得られた。

【００６７】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の４１から４時間後には２９になりさらに２４時間後には１２になり、接触角の減少はみられたが特に優れたものではなかった。

【００６８】

【比較例４】インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを１０：９０：０（モル％）とした以外は比較例１と同様に行った。均質できれいにパターニングされた膜厚９７ｎｍの光触媒膜付きガラスが得られた。

【００６９】耐トラバース性試験の結果、得られた該薄膜は非常に強固で剥離、傷はみられなかった。光触媒活性を評価した結果、水の接触角が照射前の３０から４時間後には１３になりさらに２４時間後には９になり、接触角の減少はみられたが特に優れたものではなかった。

【００７０】

【比較例５】Ｔｉアルコキシドを用いず、インキ中のＴｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを０：１０：９０：０（モル％）とした以外は実施例７と同様に行った。耐トラバース性試験の結果、得られた該薄膜は非常に脆く剥離がみられた。

【００７１】

【比較例６】インキ中のＴｉアルコキシド：酸化チタン

微粒子：シリカゾル：コロイダルシリカを０：５０：５０：０（モル％）とした以外は比較例５と同様に行った。耐トラバース性試験の結果、得られた該薄膜は非常に脆く剥離がみられた。

【００７２】

【比較例７】インキ中のＴｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを０：９０：１０：０（モル％）とした以外は比較例５と同様に行った。耐トラバース性試験の結果、得られた該薄膜は非常に脆く剥離がみられた。

【００７３】

【比較例８】反応の終結した酸化チタン微粒子の含有量を増し、インキ中のＴｉアルコキシド：酸化チタン微粒子：シリカゾル：コロイダルシリカを３０：７０：０：０（モル％）とした以外は実施例１と同様に行った。均質できれいにパターニングされた膜厚７１ｎｍの光触媒膜付きガラスが得られた。

【００７４】耐トラバース性試験の結果、得られた該薄膜は脆く著しい傷がみられた。光触媒活性を評価した結果、水の接触角が照射前の７２から４時間後には２になり、さらに２４時間後には１になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００７５】

【比較例９】コロイダルシリカの含有量を増し、インキ中のＴｉアルコキシド：シリカゾル：コロイダルシリカを３０：０：７０（モル％）とした以外は実施例４と同様に行った。均質できれいにパターニングされた膜厚７８ｎｍの光触媒膜付きガラスが得られた。

【００７６】耐トラバース性試験の結果、得られた該薄膜は脆く著しい傷がみられた。光触媒活性を評価した結果、水の接触角が照射前の４０から４時間後には１になり、さらに２４時間後には１以下になり、該光触媒膜付きガラスが非常に高い光触媒活性を有することが確認できた。

【００７７】

【表１】

| | インキ主成分組成(モル%) | | | | | 光触媒活性(°) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| サンプルNo. | Tiアルコキシド | Ti微粒子 | シリカゾル | コロイダルシリカ | 下地層 | 照射前 | 4時間 | 24時間 | 評価 | 耐トラバース性 | 総合評価 |
| 実施例 1 | 90 | 10 | 0 | 0 | SiO2 | 91 | 7 | 2 | ◎ | ◎ | ◎ |
| 実施例 2 | 70 | 30 | 0 | 0 | SiO2 | 90 | 5 | ＜1 | ◎ | ◎ | ◎ |
| 実施例 3 | 70 | 30 | 0 | 0 | − | 71 | 9 | 4 | ◎ | ◎ | ◎ |
| 実施例 4 | 90 | 0 | 0 | 10 | SiO2 | 84 | 2 | ＜1 | ◎ | ◎ | ◎ |
| 実施例 5 | 70 | 0 | 0 | 30 | SiO2 | 73 | 2 | 1 | ◎ | ◎ | ◎ |
| 実施例 6 | 50 | 0 | 0 | 50 | SiO2 | 80 | 2 | 1 | ◎ | ◎ | ◎ |
| 実施例 7 | 40 | 40 | 20 | 0 | SiO2 | 70 | 3 | 1 | ◎ | ◎ | ◎ |
| 実施例 8 | 60 | 0 | 20 | 20 | SiO2 | 42 | 6 | − | ◎ | ◎ | ◎ |
| 実施例 9 | 60 | 0 | 20 | 20 | SiO2 | 43 | 10 | − | ○ | ◎ | ○ |
| 実施例10 | 60 | 0 | 20 | 20 | TiO2-SiO2 | 45 | 10 | − | ○ | ◎ | ○ |
| 実施例11 | 70 | 0 | 10 | 20 | SiO2 | 50 | 6 | − | ◎ | ◎ | ◎ |
| 実施例12 | 45 | 0 | 35 | 20 | SiO2 | 41 | 3 | ＜1 | ◎ | ◎ | ◎ |
| 実施例13 | 45 | 0 | 35 | 20 | − | 41 | 3 | ＜1 | ◎ | ◎ | ◎ |
| 実施例14 | 10 | 0 | 80 | 10 | SiO2 | 24 | 10 | 5 | ○ | ◎ | ○ |
| 比較例 1 | 45 | 0 | 55 | 0 | SiO2 | 45 | 25 | 7 | × | ◎ | × |
| 比較例 2 | 75 | 0 | 25 | 0 | SiO2 | 86 | 32 | 6 | × | ◎ | × |
| 比較例 3 | 31 | 0 | 69 | 0 | SiO2 | 41 | 29 | 12 | × | ◎ | × |
| 比較例 4 | 10 | 0 | 90 | 0 | SiO2 | 30 | 13 | 9 | × | ◎ | × |
| 比較例 5 | 0 | 10 | 90 | 0 | SiO2 | − | − | − | − | × | × |
| 比較例 6 | 0 | 50 | 50 | 0 | SiO2 | − | − | − | − | × | × |
| 比較例 7 | 0 | 90 | 10 | 0 | SiO2 | − | − | − | − | × | × |
| 比較例 8 | 30 | 70 | 0 | 0 | SiO2 | 72 | 2 | 1 | ◎ | × | × |
| 比較例 9 | 30 | 0 | 0 | 70 | SiO2 | 40 | 1 | ＜1 | ◎ | × | × |

【００７８】

【発明の効果】本発明の光触媒膜形成用インキは、反応の終結した酸化物微粒子を含有させてあるので、インキが極めて安定であるとともに、インキ自身のポットライフが長くなり、スクリーン印刷などの印刷法のインキとして優れると共に、本発明の光触媒膜形成用インキを用いて作製した光触媒膜は、その他の成膜方法のディップコート法、ロールコート法、スピンコート法などに比べて光触媒活性、耐摩耗性で遜色がなく、低コストで高耐久な優れたものが得られる。

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